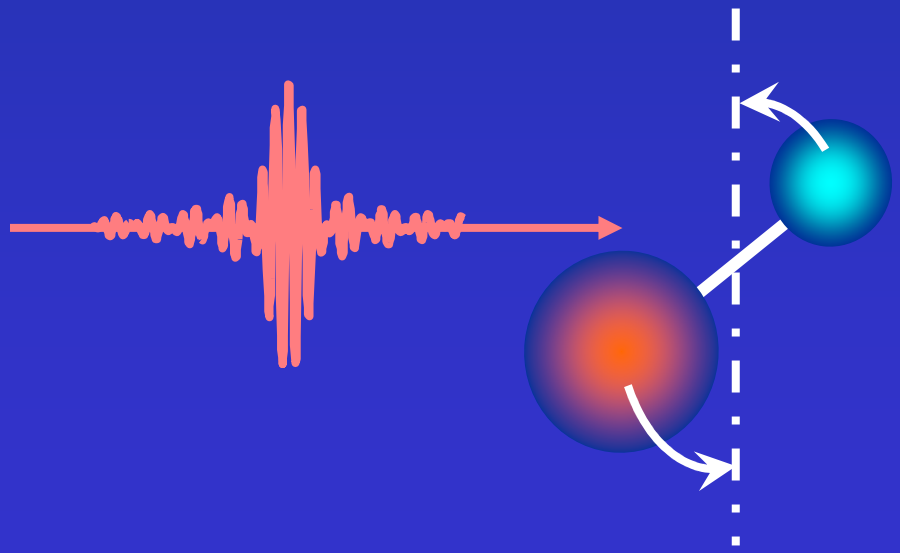
Towards the transient orientation of linear molecules

Thibault Vogt

October, 15 2007



History : alignment and orientation in dilute gases

- **Static fields**
  - **Quadrupole field and Hexapole field focusing : Stark effect used to select a rotational state $|J,M_J\rangle$ of a molecule from a thermal mixture of rotational states**

    Diatomic molecules : *Zeitschrift für Physics, 141 : 6 (1955)*

    Symmetric top molecules : *JCP, 42 : 767 (1965)*
  - **Brute Force orientation : strong static electric field to orientate molecules with a big dipole moment**

    JCP, 93 : 4779 (1990)
- **Laser fields**
  - **Adiabatic alignement : intense laser electric field, pulse whose duration is much longer than the rotational period of the molecule**

    JCP, 104 : 3 (1996)
  - **Diabatic alignment : femtosecond laser electric field pulse, duration smaller than the rotational period of the molecule, field-free alignment**

    Phys. Rev. Let. 87 : 15 (2001)
  - **Transient Orientation ?**

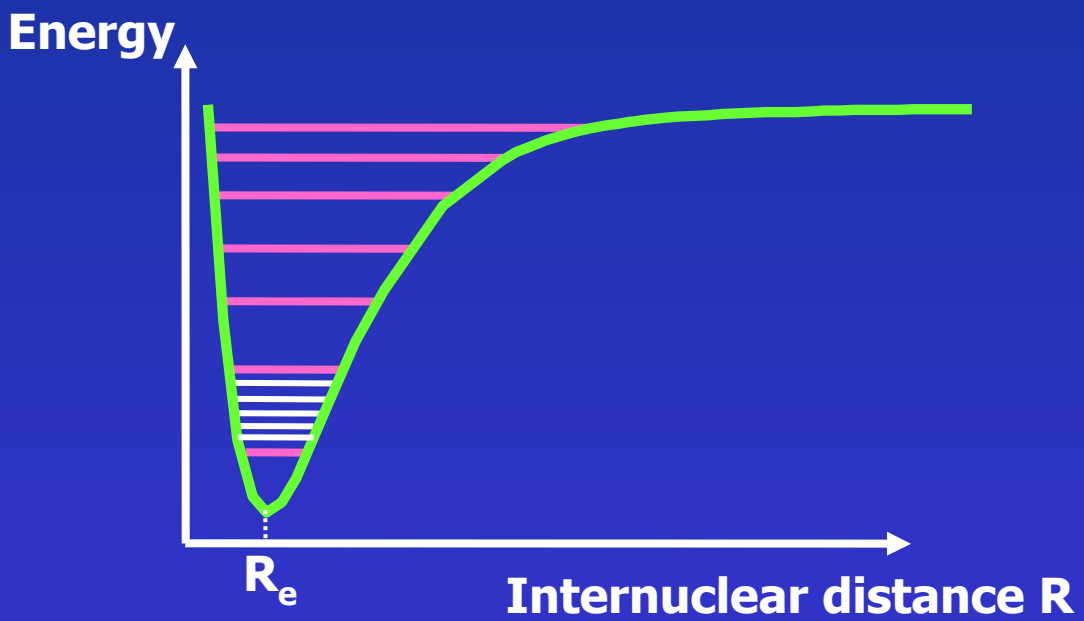
Outline

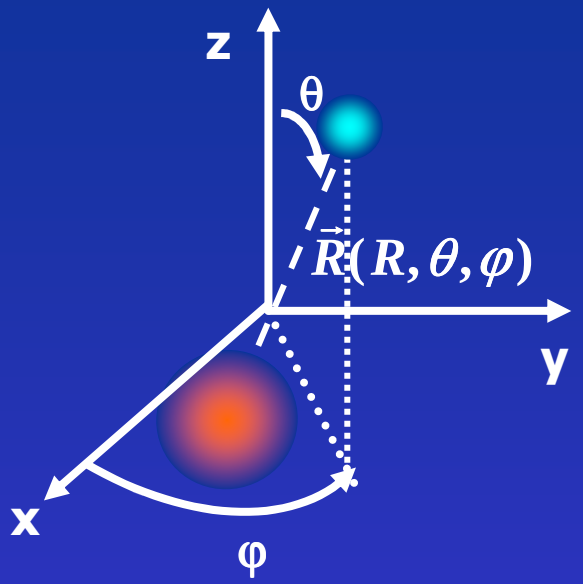
- Orientation with static fields
  Orientation and alignment with laser fields
  $\Rightarrow$ femtochemistry, interferometry, quantum information, atosecond pulses…
- Transient Orientation of linear molecules
  - Computations
  - Half-cycle pulses
  - Asymetric femtosecond pulses
  - Perspectives, status of the AMO experiments

Orientation/Alignment : signification

$$W_s = W_{el} + W_{vib} + W_{rot}$$

$$|\Psi_s\rangle = |\Psi_{el}\rangle |\Psi_{vib}\rangle |\Psi_{rot}\rangle$$





Orientation :

$$\vec{R}.\vec{u}_z \propto R_e \cos\theta$$

Alignment :

$$\left|\vec{R}.\vec{u}_z\right|^2 \propto R_e^2 \cos^2\theta$$

For singlet molecules (Λ=0)

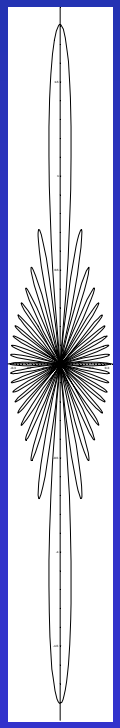
$$\Psi_{rot} = \left\langle \vec{R} \middle| J,M \right\rangle = Y_J^M(\theta,\varphi) \qquad W_{rot} = B\,J(J+1)$$

State selection

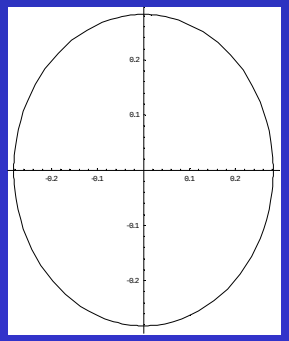
Graph of the Stark energy change $W_{|J,M\rangle}(E^2)$

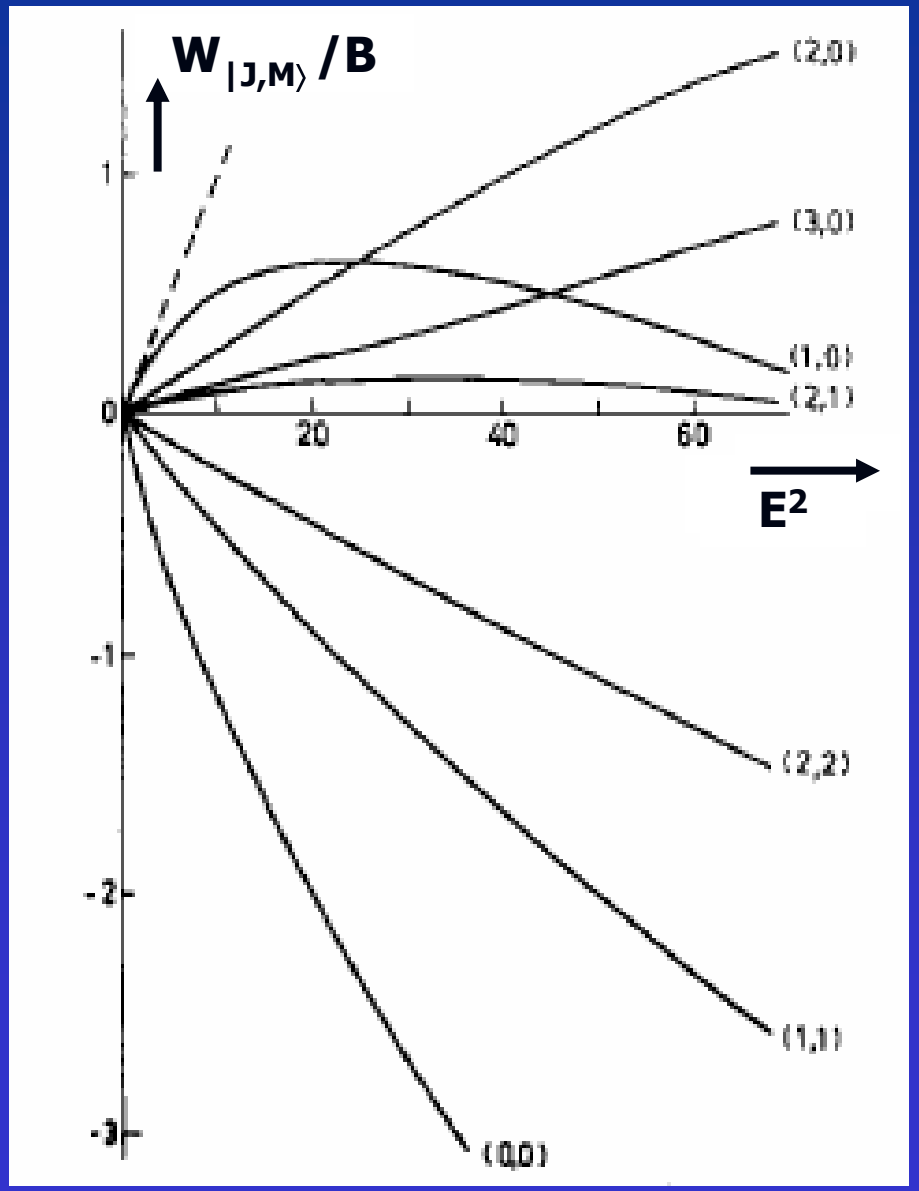
$$\vec{F} = -\overrightarrow{grad}(W_{|J,M\rangle})$$

$$|J,M\rangle = |20,0\rangle$$

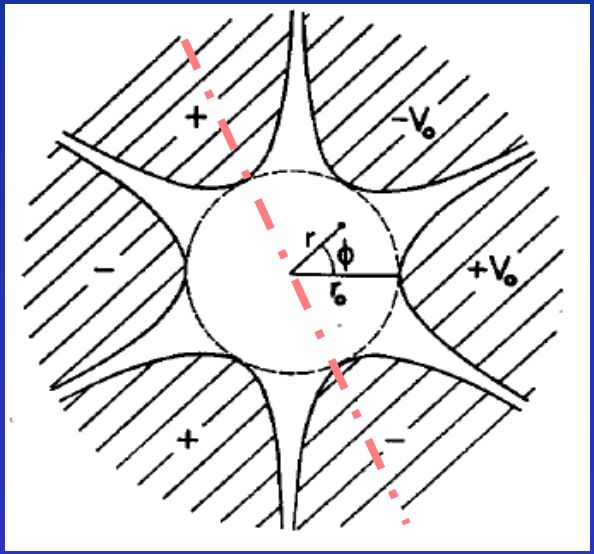


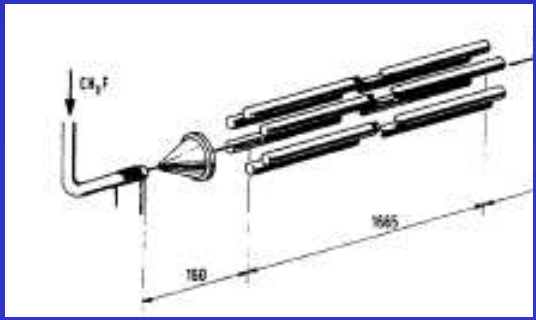
$$|J,M\rangle = |0,0\rangle$$





Hexapole focusing



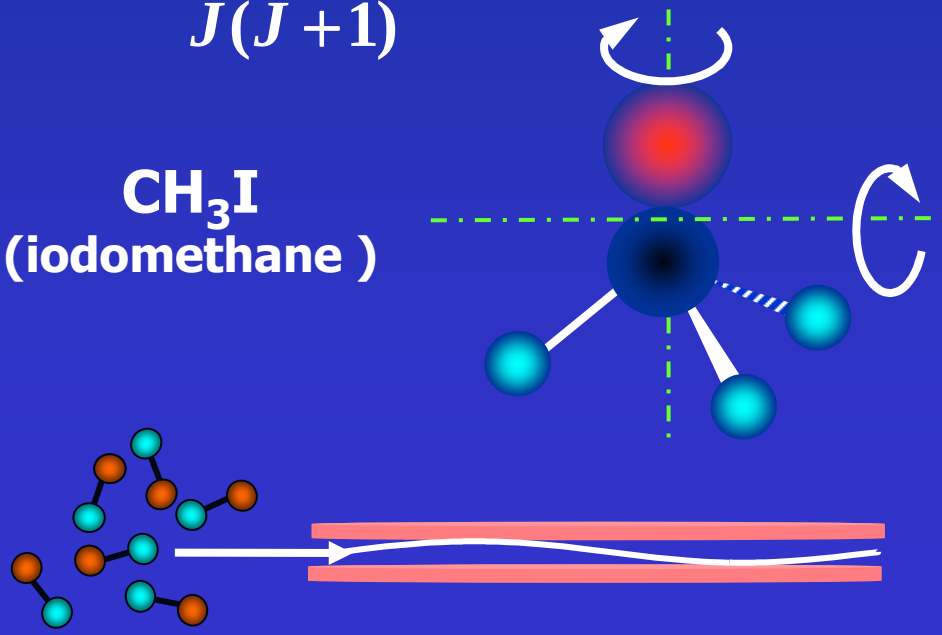


Used for symmetric top molecules

$$\left|\Psi_s\right\rangle \propto \left|J,K,M\right\rangle$$

$$\vec{F} \propto \frac{KM}{J(J+1)}\vec{r}$$

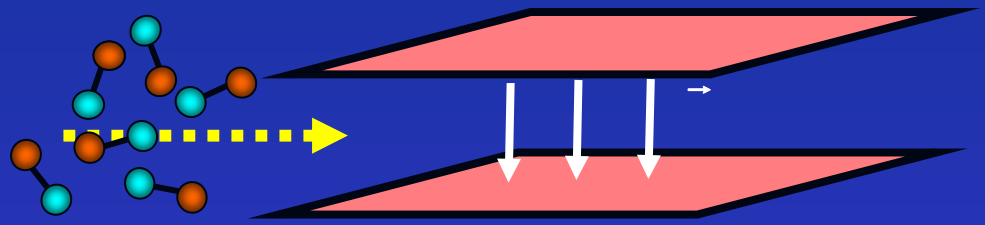
CH_3I
(iodomethane)



Brute force orientation

Interaction energy of a polar molecule with a strong static electric field

$$-\vec{\mu}\cdot\vec{E}_s = -\mu_0 E_s \cos\theta$$



Classical picture : torque exerted on the molecule, alignment of the permanent dipole moment on the field

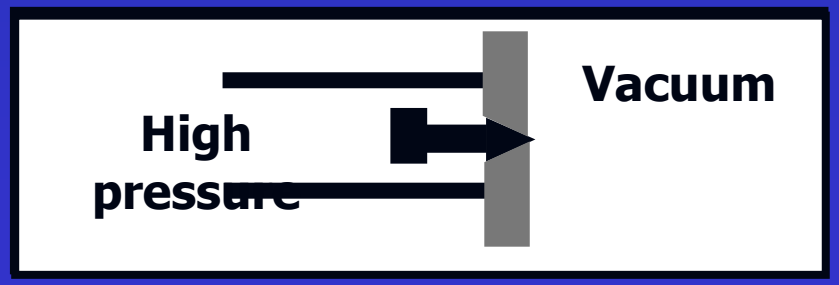
Possibility with symmetric top molecules, but also singlet molecules

Necessity of a very strong static field. Example : KCl, μ_0=10.27 D, E_s~30 kV/cm

Also very small temperatures (supersonic molecular beams)

Supersonic jet : rotational cooling

$$P(|J,M\rangle) = e^{-BJ(J+1)/(kT)}$$



Stereodynamics studies

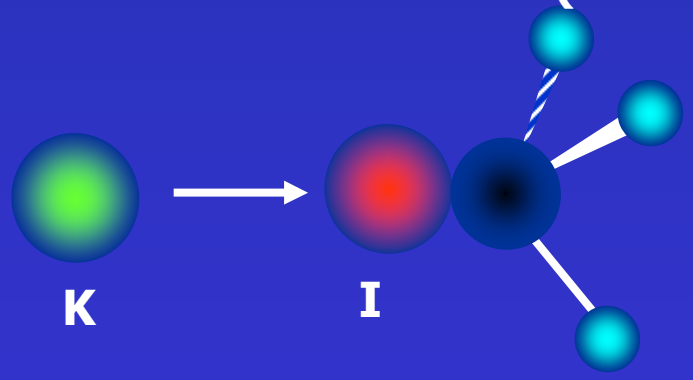
Studies on the steric effect (modification of reactions depending on the geometry and the presence of different chemical groups in molecules)

Collisionnal studies, head versus tail preferential reactions

$$K + CH_3I \rightarrow KI + CH_3$$

CH_3I (iodomethane)

Preferential reaction

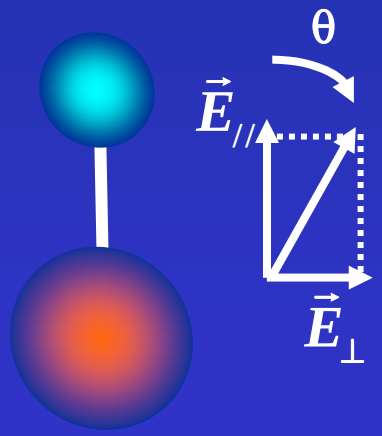


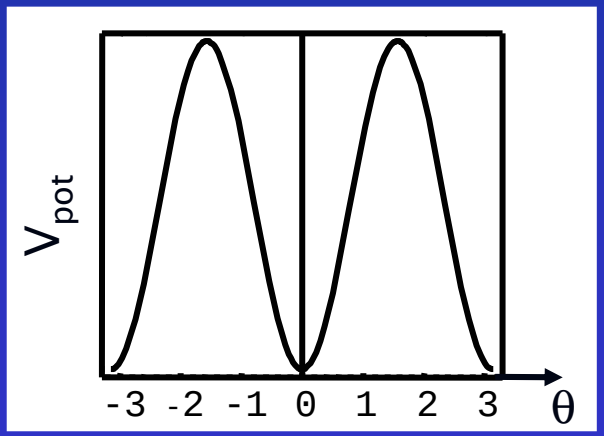
Laser induced alignment

Strong static field replaced by a strong non-resonant laser field

$$H_{eff} = -\frac{1}{2} \sum_{i,j=x,y,z} \alpha_{ij} E_i E_j$$

$$H_{eff} = -\frac{1}{4}(\alpha_{//} - \alpha_{\perp}) Cos^2\theta \, E_0^2$$





$\Delta\alpha = 6$ *for* N_2

Adiabatic alignment

Condition of adiabaticity

$$\nu_{rot}(J) = \frac{B\,J(J+1)}{h}$$

$$T_p \gg T_{rot}(1) = \frac{1}{\nu_{rot}(1)} = \frac{\pi\hbar}{B}$$

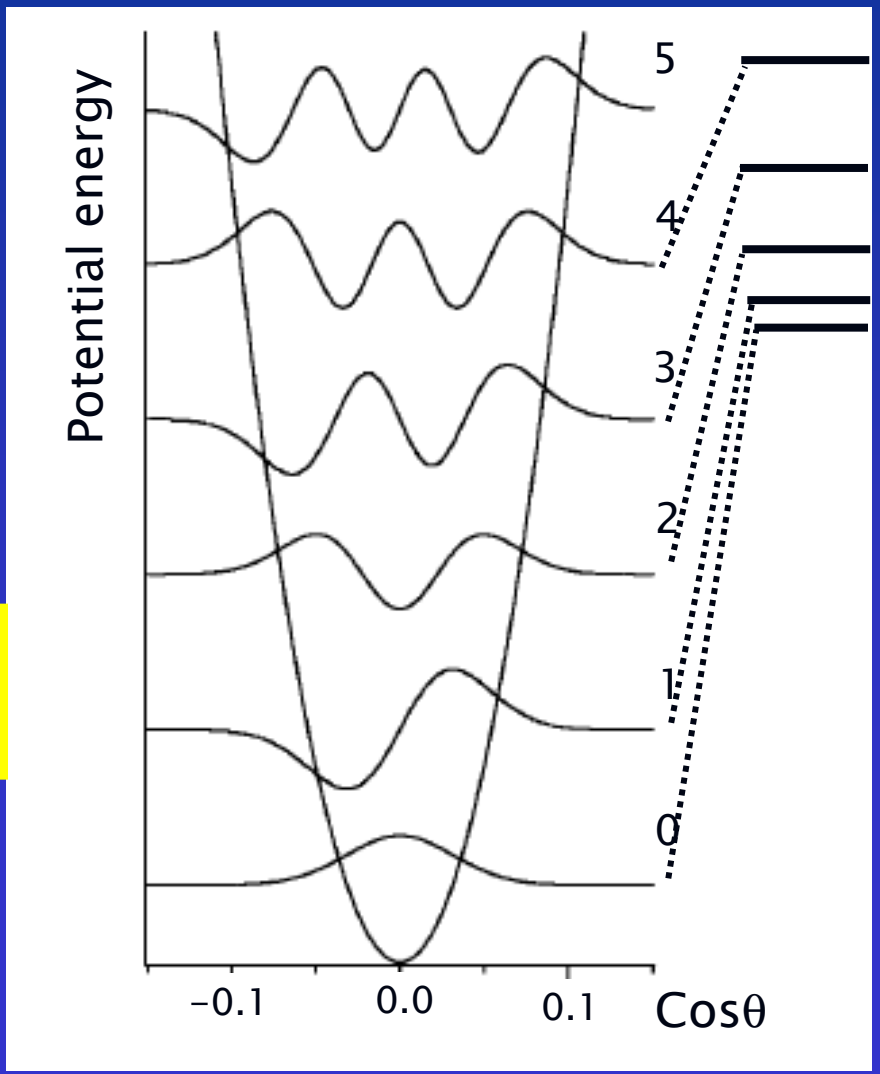
Pendular states observation for symmetric top molecules

J. Chem. Phys. ***104*** *: 3 (1996)*

« Adiabatic » orientation : Strong laser field+ static field

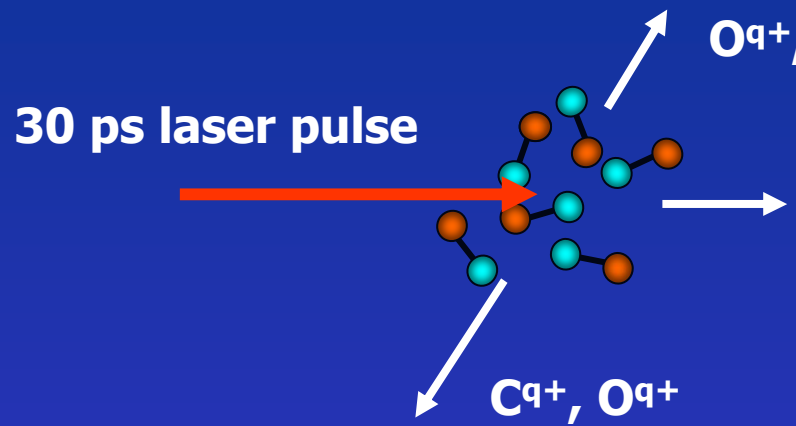
$$H_{eff} = -\vec{\mu_0}.\vec{E_S} - \frac{1}{4}(\alpha_\perp - \alpha_{//})\cos^2\theta\, E_0^2 - \frac{1}{4}\alpha_{//} E_0^2$$

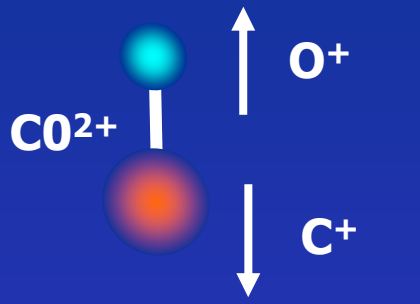
Phys. Rev. Let. , 90 : 083001 (2003)



CO ionization

D. Normand et al., J. Phys. B: At. Mol. Opt. Phys. 25, L497 (1992)

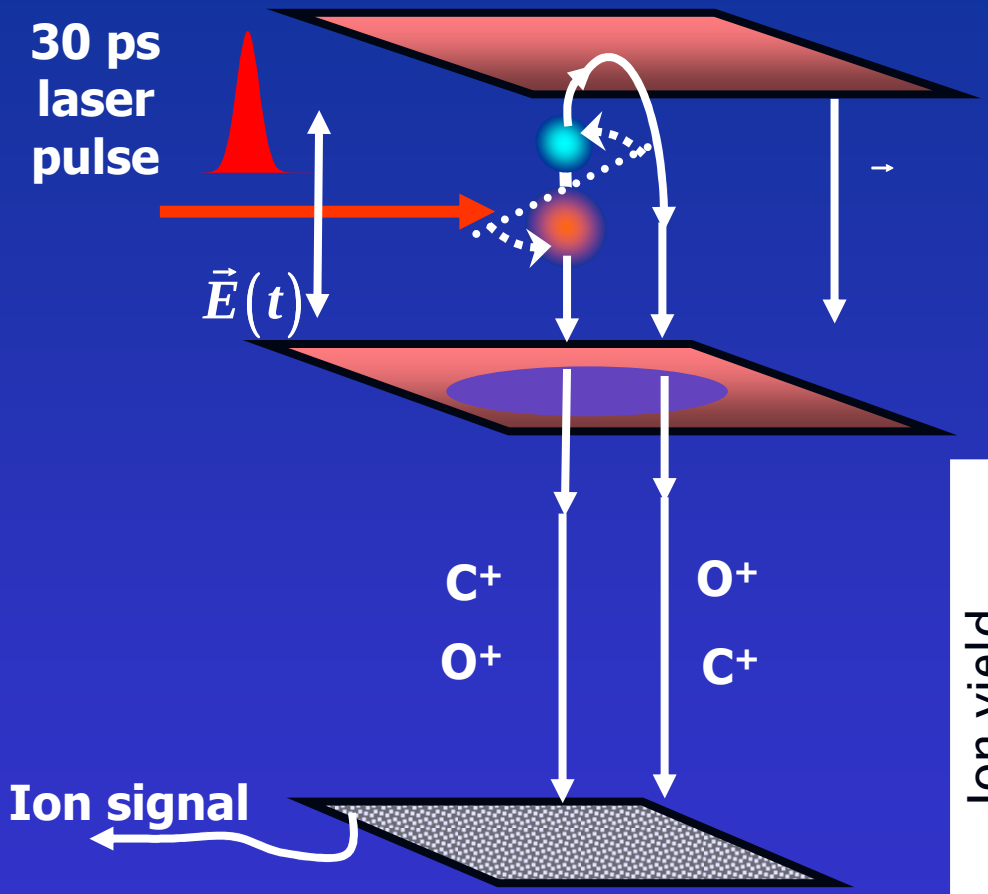


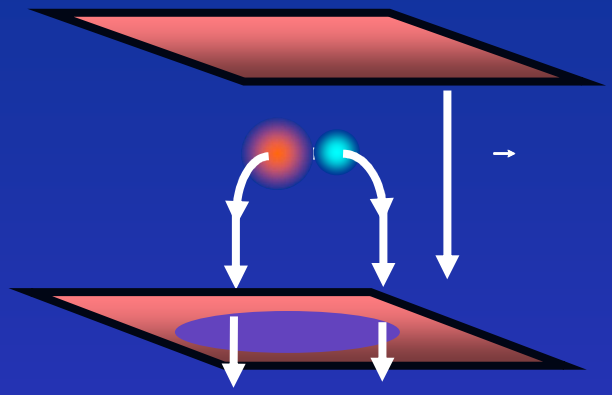


Coulomb explosion

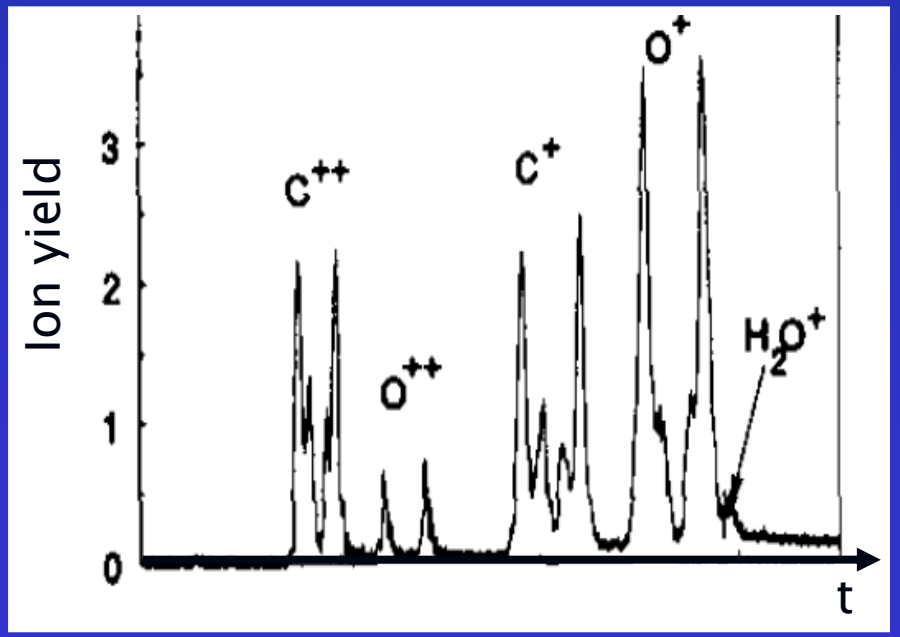
Decay path	Energy released (eV)	Branching ratio (%)
(1) $CO^+ \rightarrow C^+ + O$	1.2	11
(2) $CO^+ \rightarrow C + O^+$	2	15
(3) $CO^{2+} \rightarrow C^+ + O^+$	6	24
(4) $CO^{3+} \rightarrow C^{2+} + O^+$	10	39
(5) $CO^{3+} \rightarrow C^+ + O^{2+}$	11	8
(6) $CO^{4+} \rightarrow C^{2+} + O^{2+}$	20	3

Experimental observation : TOF spectroscopy

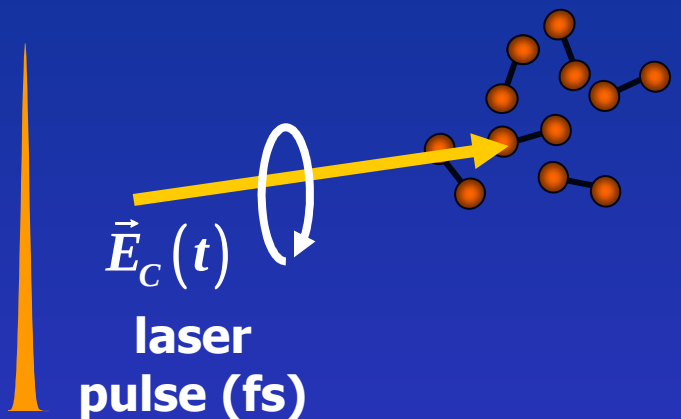


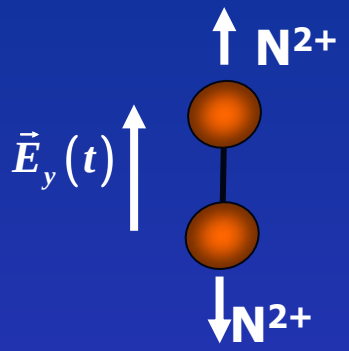


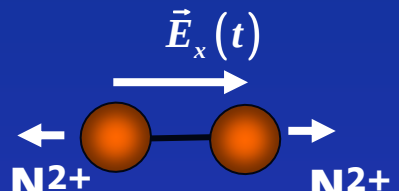
Alignment ?

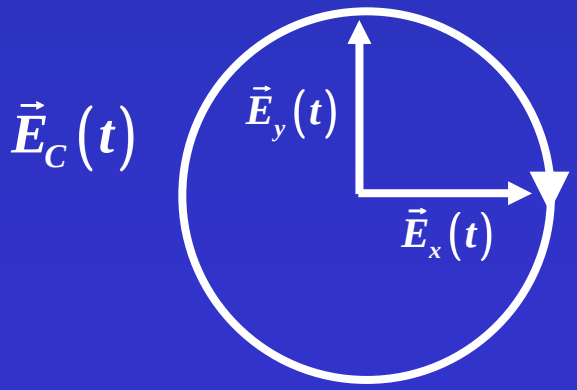


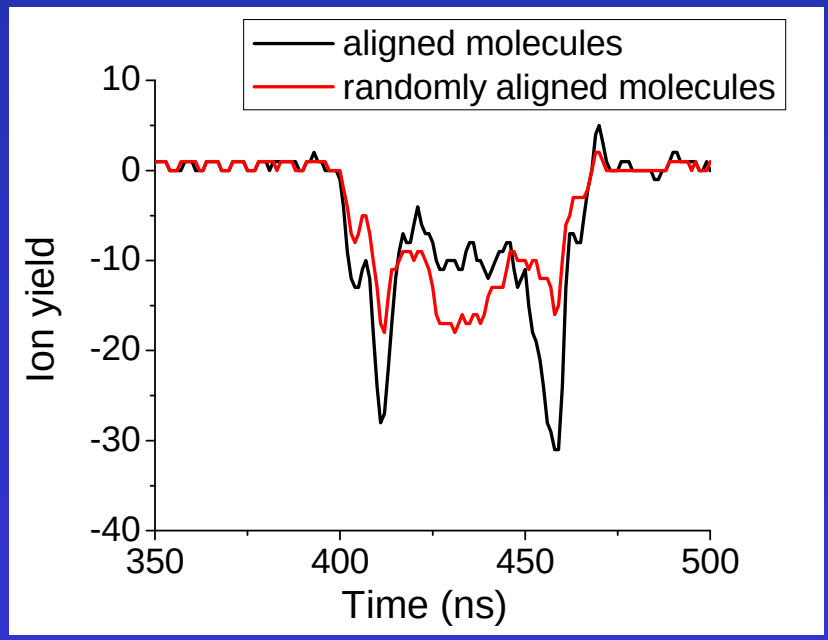
Detection (N_2)





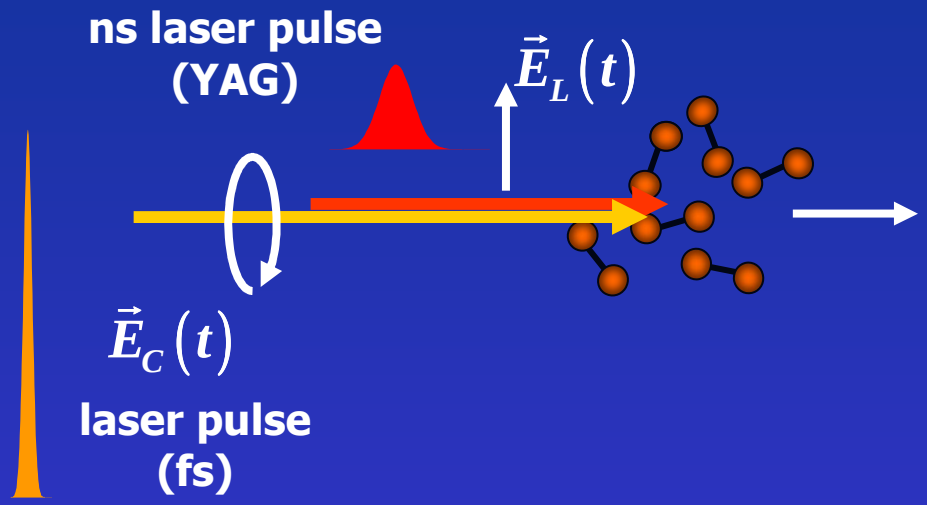


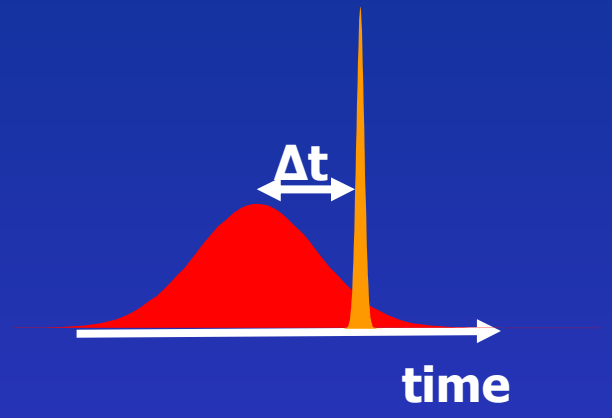


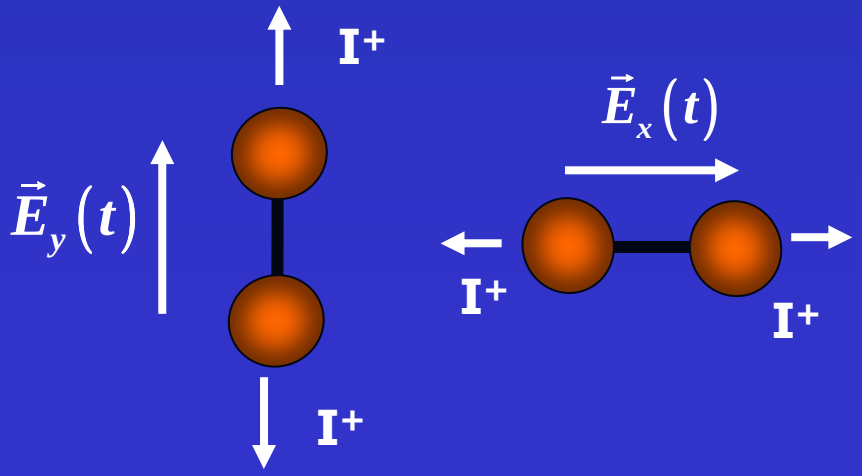


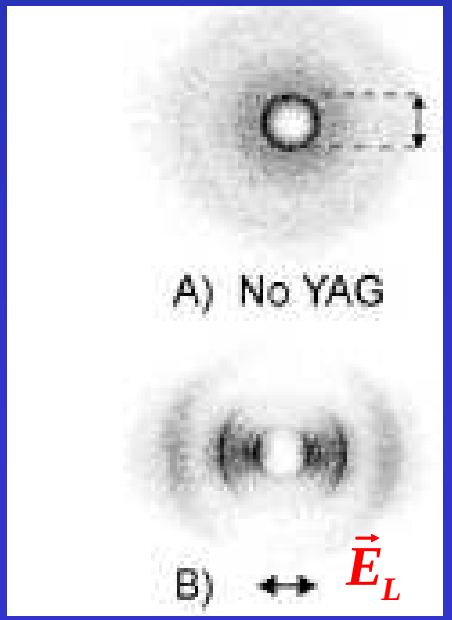
Adiabatic alignment of Diiodine (I_2)

JCP, 110 : 10235 (1999)



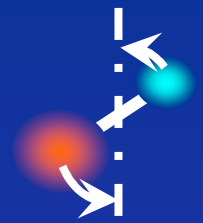






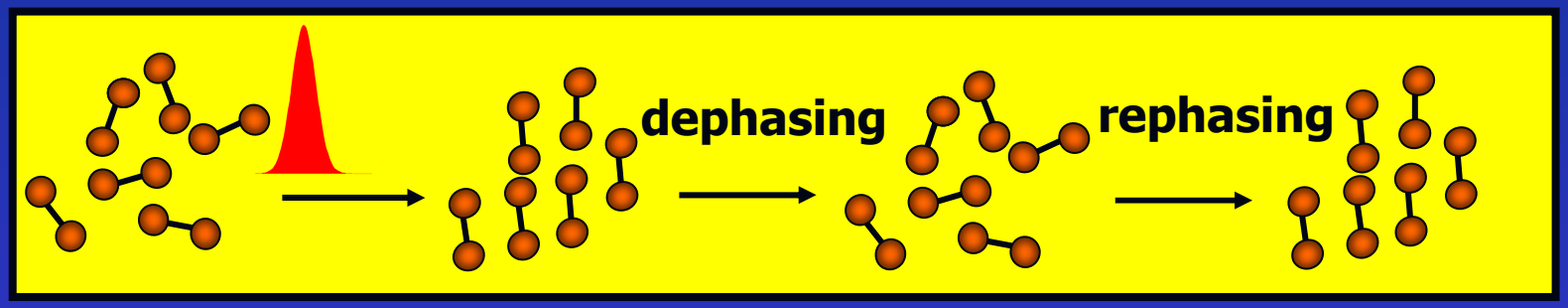
Diabatic alignment

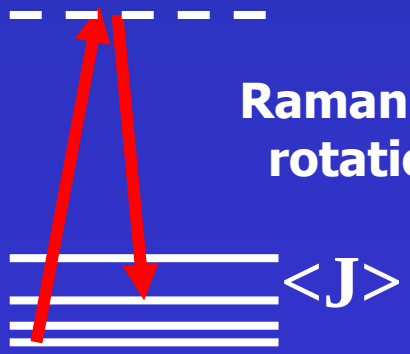
$$H_{eff} = \frac{1}{4}(\alpha_{\perp} - \alpha_{//})\,Cos^2\theta\,E_0^2 - \frac{1}{4}\alpha_{\perp}E_0^2$$



Short Pulse $\rightarrow$ Impulsive Angular Kick

$$\frac{d\vec{p}}{dt} \propto -Sin2\theta\,E_0^2\,\overrightarrow{u_\theta}$$





Raman excitation of rotationnal states

$$W_J = B\,J(J+1)$$

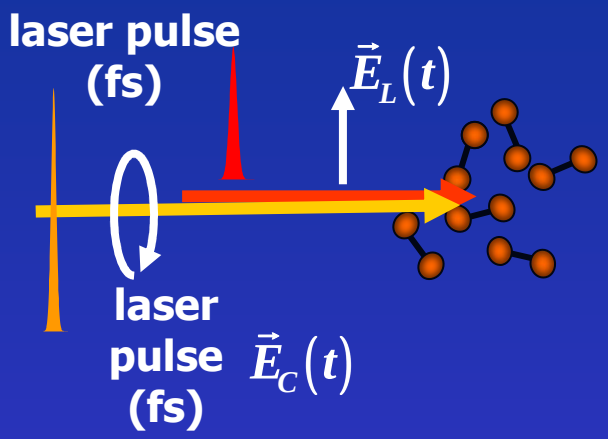
$$\left|J_0, M_0\right\rangle \Rightarrow \Psi(t) = \sum_{J,M} c_J e^{-\frac{W_J t}{\hbar}} \left|J, M\right\rangle$$

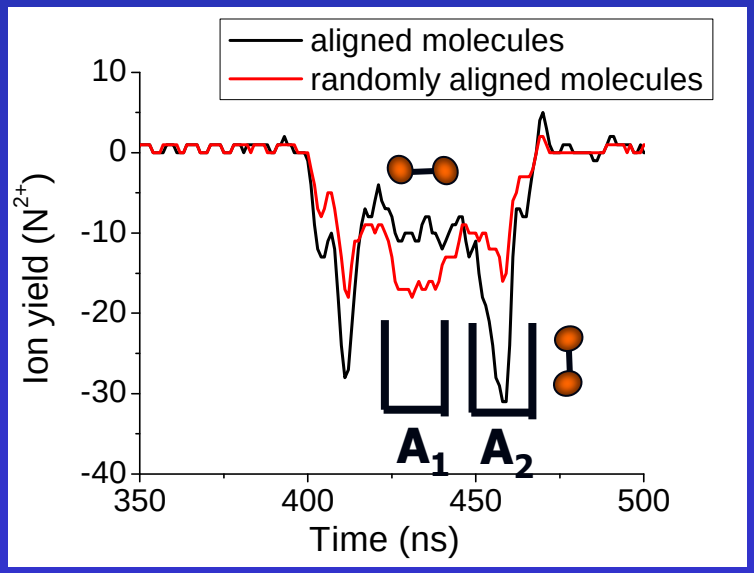
Wavepacket excitation : revivals

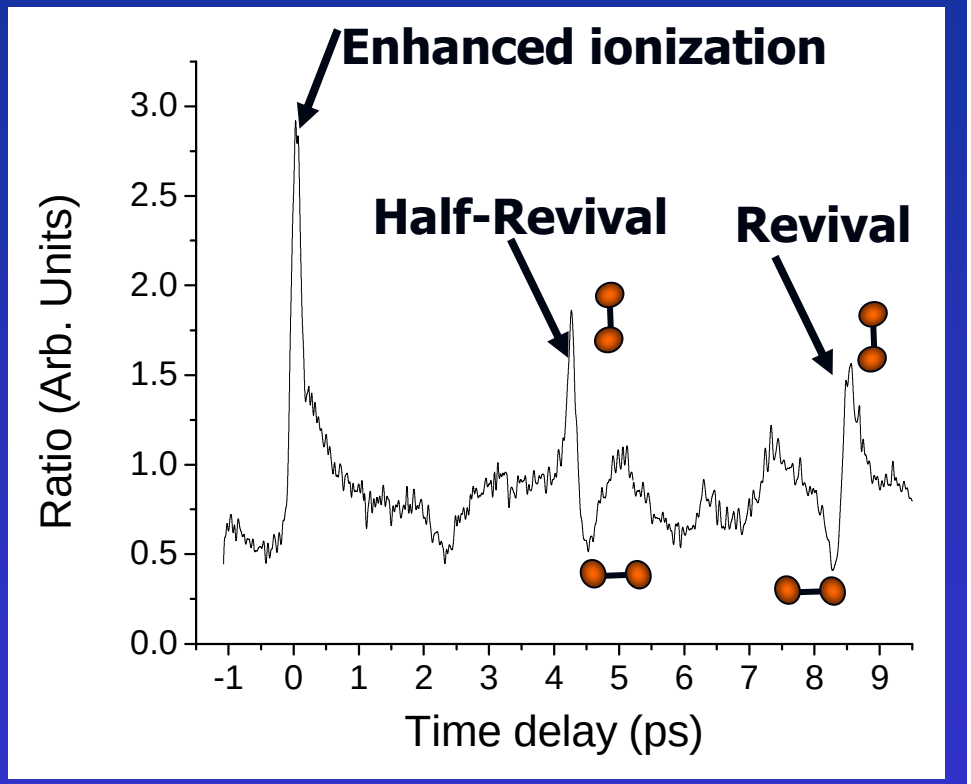
$$\nu_J = k(J)\frac{2B}{h} \Rightarrow \tau_R = \frac{\pi\hbar}{B}$$

Diabatic alignment

Phys. Rev. Let., 87 : 153902 (2001)

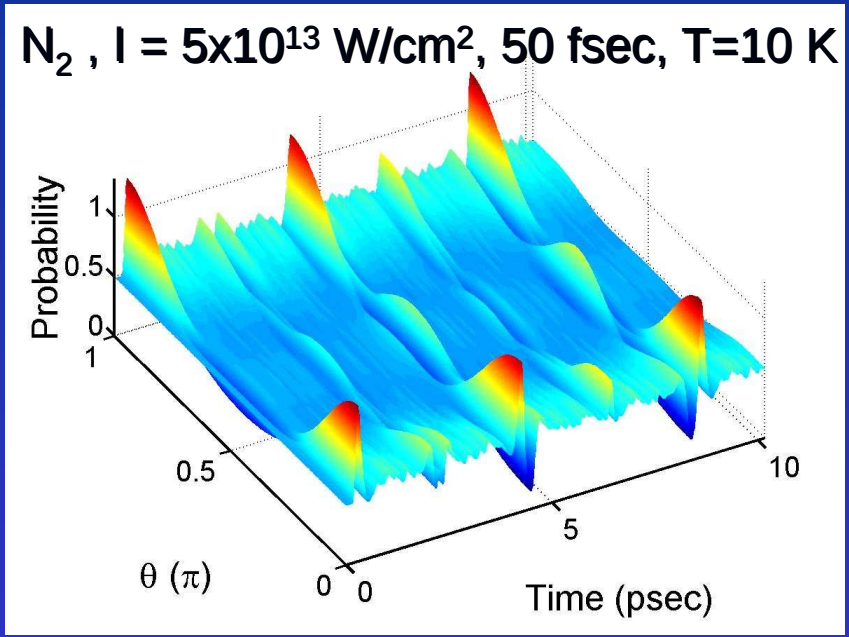


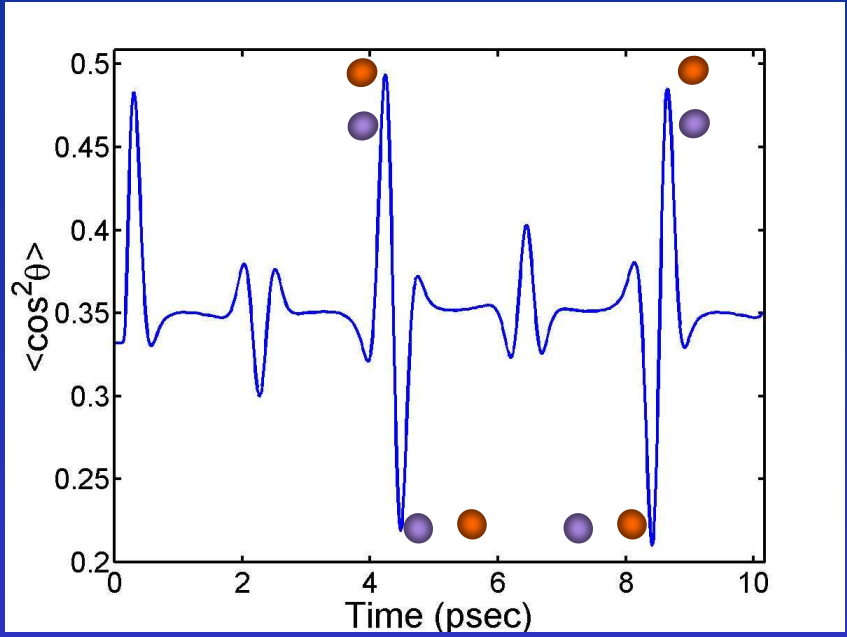




$$\text{Ratio} = \frac{A_2 - A_1}{A_1 + A_2}$$

Diabatic alignment





Non-Zero Temperature: $P_{|J,M\rangle} \sim \exp[-J(J+1)B/k_BT]$

At high T, high Bohr frequencies, Centrifugal distortion

$\rightarrow$ Reduced Net Alignment

Applications

Preferential dissociation, Fragments selection

Control : pulse shaping

3D alignment

Lithography : Focusing and orienting molecules

Orientation of molecules and quantum information processing

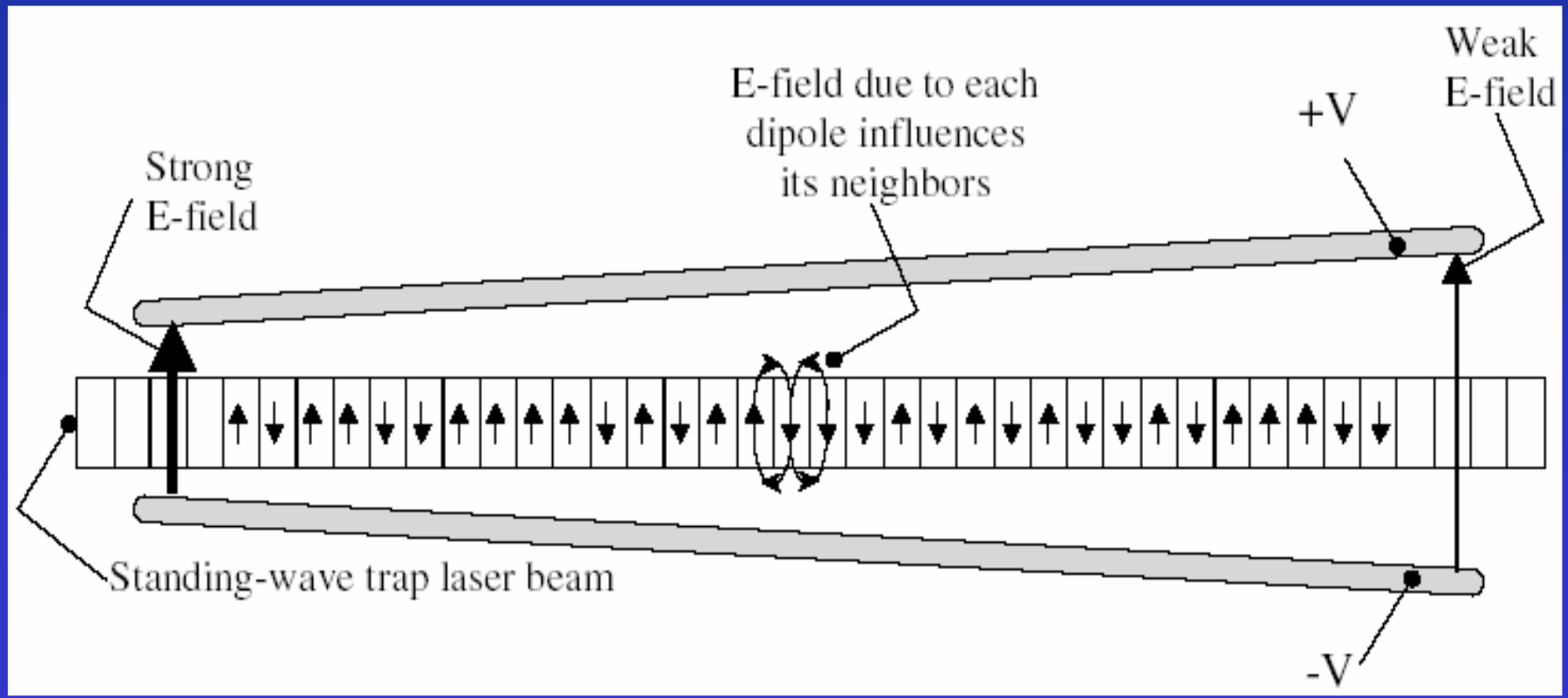
Rotational temperature measurement

Attosecond pulses, rescattering experiments

Tomographic imaging of molecular orbitals

Orientation of molecules and quantum information processing

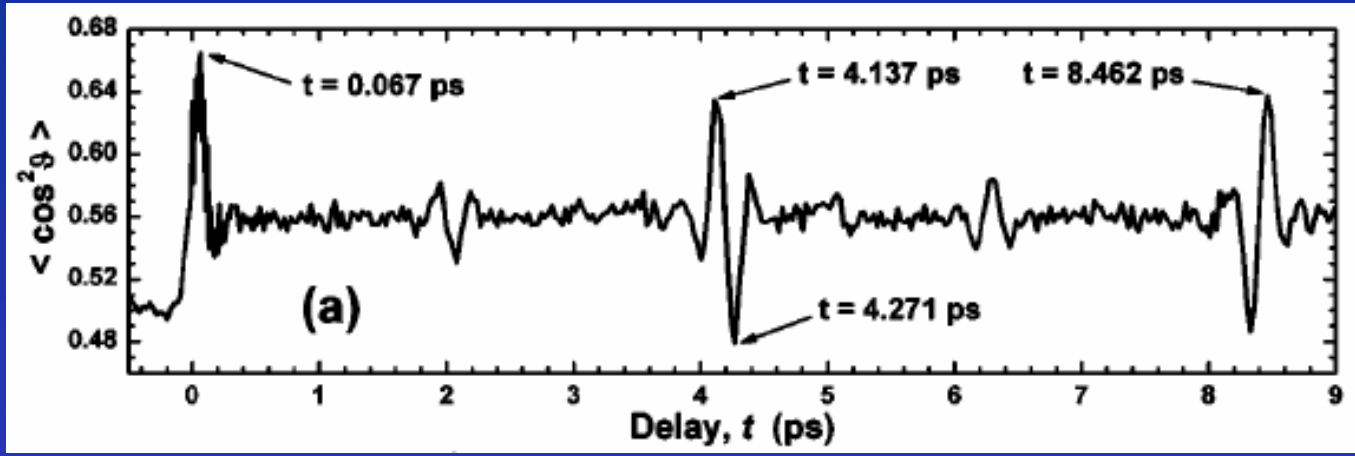
Stark addressing of individual trapped polar oriented molecules (qubit), interaction between the qubits driven by the dipole-dipole interaction



D. DeMille, PRL 88, 067901

Rotational temperature analysis

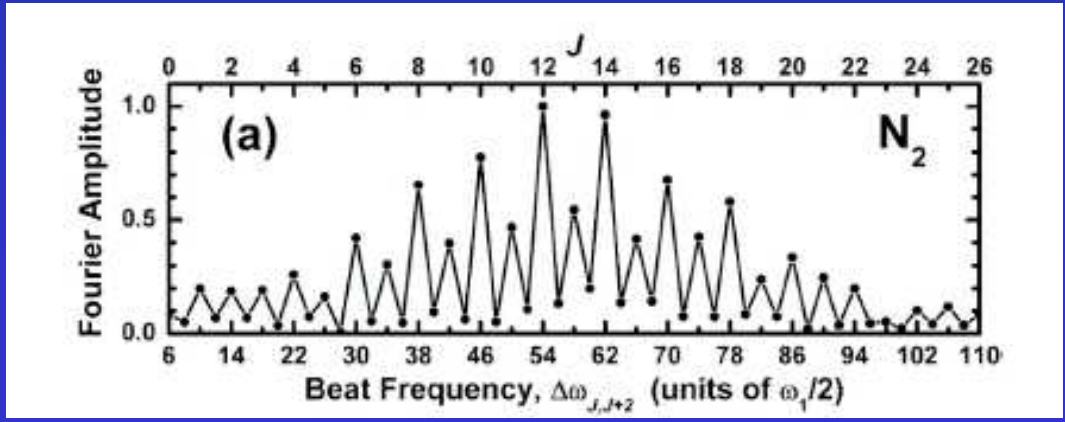
Phys. Rev. A ***68*** *: 023406 (2003)*



Fourier analysis

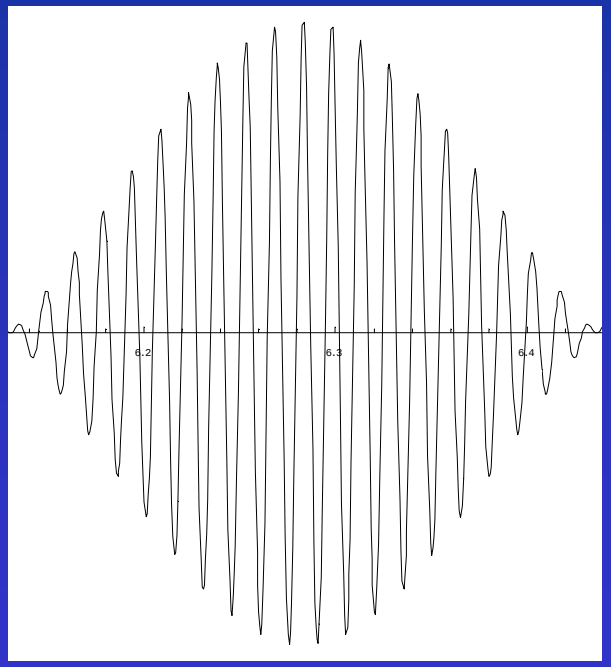
Amplitude of the states after excitation

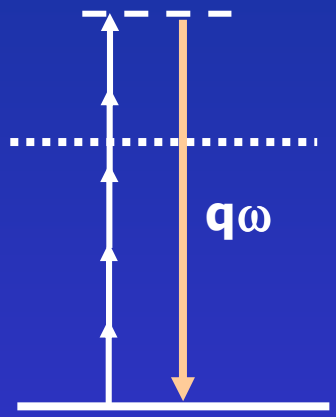
$$P\left(\left|J,M\right\rangle\right) = S(J)\, e^{-BJ(J+1)/(kT)}$$

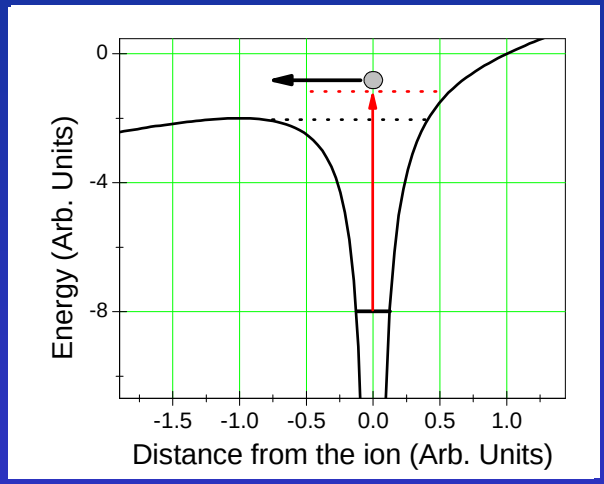


Attosecond pulses, rescattering experiments

Attosecond pulses from High Harmonic generation
Science, 292 : 1689 (2001)





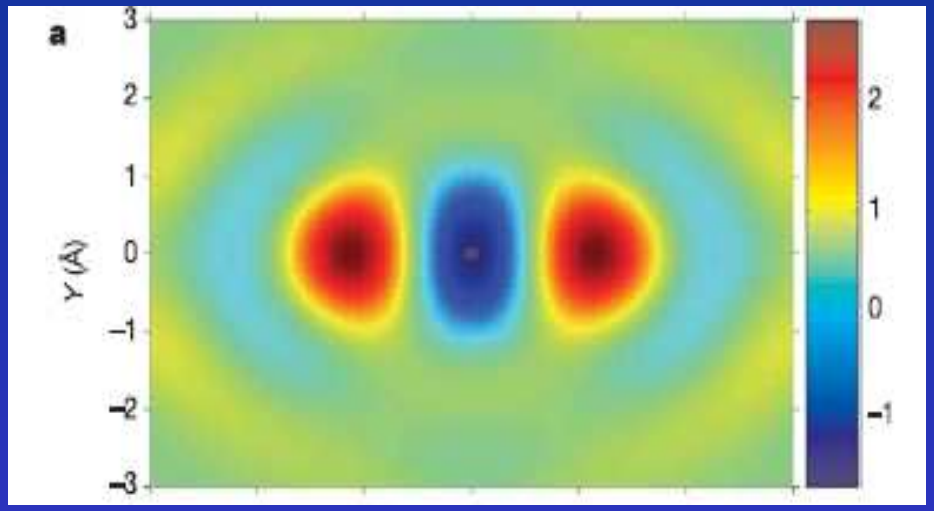


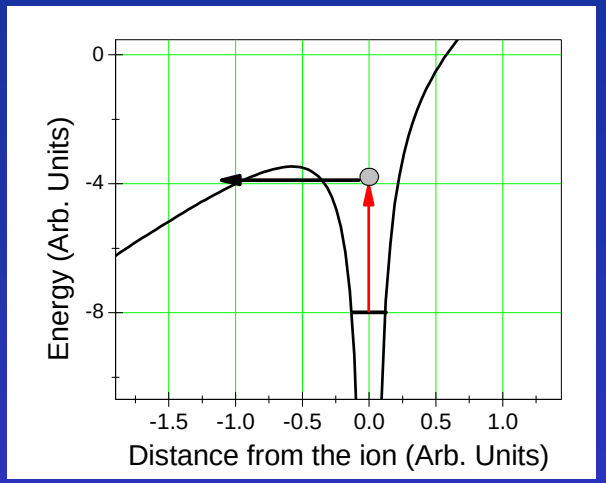
Symmetry properties ⇒ odd harmonics for atoms

Even harmonics for non centrosymmetric molecules

Tomographic imaging of molecular orbitals

Nature, 432 : 867 (2004)





Reconstructed of N2 in its ground state HOMO (highest occupied molecular orbital)
Experimental HHG (High Harmonic generation) spectrum (dependence with alignment)

Intermediate conclusion

- Orientation in a static field
- Adiabatic alignment
- Diabatic (field-free) alignment

- Field-free orientation

Theory

Interaction energy of a molecule with an electric field

$$H = H^{(0)} + V$$

$$= H^{(0)} - \vec{\mu} \,.\, \vec{E} - \sum_{\alpha,\beta=x,y,z} \frac{1}{3} \Theta_{\alpha\beta} \frac{\partial E_\beta}{\partial \alpha} - \vec{m}.\vec{H} - \ldots$$

Dipolar moment operator

$$\vec{\mu} = \sum_i e_i \vec{r}_i = \sum_{\alpha=x,y,z} \mu_\alpha = \sum_\alpha \sum_i e_i r_{i_\alpha}$$

Quadrupolar moment operator

$$\Theta_{\alpha\beta} = \frac{1}{2} \sum_i e_i \left(3 r_{i_\alpha} r_{i_\beta} - r_i^2 \delta_{\alpha\beta}\right)$$

Dipolar approximation : size of the molecule << λ

Theory

Interaction energy of a molecule with a static electric field

$$H = H^{(0)} - \vec{\mu} \,.\, \vec{E} \qquad \vec{\mu} = \sum_{i=x,y,z} \mu_i = \sum_i \sum_n e_n r_{n_i}$$

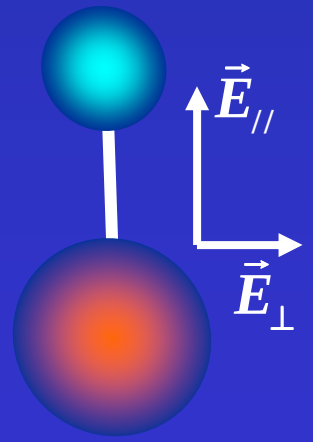
Result from the perturbation theory, for a given state Ψ :

$$W = \langle \Psi | H | \Psi \rangle = W^{(0)} - \mu_i^{(0)} E_i - \frac{1}{2}\alpha_{ij} E_i E_\beta - \frac{1}{6}\beta_{ijk} E_i E_j E_k - \ldots$$

Linear Polarisability : α_{ij}

Diatomic molecules : $-\frac{1}{2}\alpha_{//} E_{//}^2 - \frac{1}{2}\alpha_{\perp} E_{\perp}^2$

First Hyperpolarisability β_{ijk}



Interaction energy of a molecule with a periodic electric field

$$H = H^{(0)} - \vec{\mu} \cdot \vec{E}(t) \qquad \vec{\mu} = \sum_{i=x,y,z} \mu_i = \sum_i \sum_n e_n r_{n_i}$$

$$W = \langle \Psi | H | \Psi \rangle = W^{(0)} - \overline{\mu_i^{(0)} E_i} - \overline{\frac{1}{2} \alpha_{ij} E_i E_j} - \overline{\frac{1}{6} \beta_{ijk} E_i E_j E_k} - \ldots$$

"Explanation" : Floquet theorem ⇒ wavefunction expanded in Fourier series

$$\Psi_s = e^{\left(-iW_s t/\hbar\right)} \sum_{n=-\infty}^{\infty} C_n e^{(-in\omega t)}$$

sum of wavefunctions $C_n e^{\left(-i\left(\frac{W_s}{\hbar} + n\omega\right)t\right)}$

with $W_s = \overline{\langle \Psi_s | -\vec{\mu} \cdot \vec{E} | \Psi_s \rangle}$

$$W_s' = W_s + n\hbar\omega$$

Very weak interaction ⇒ C_0 only non negligible term ⇒ Possibility to define one energy

$$W_s' = W_s \qquad \Psi_s = e^{\left(-iW_s t/\hbar\right)} \Phi_s = e^{\left(-iW_s t/\hbar\right)} C_0$$

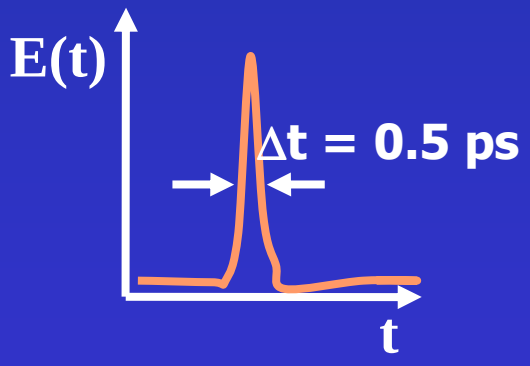
Time independent Schrodinger equation, possibility to apply time independent perturbation theory to these wavefunctions

Field–free orientation of molecules

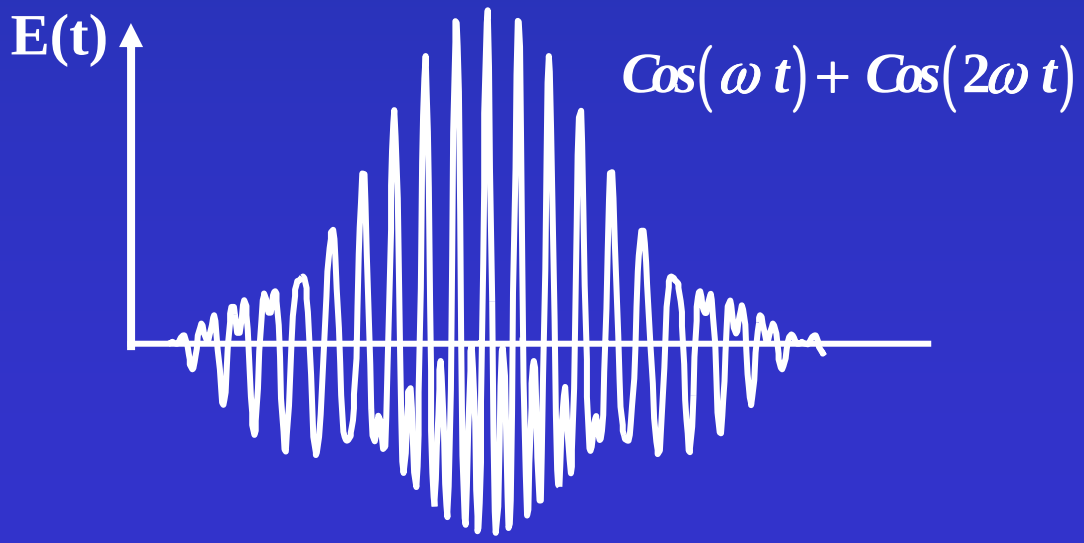
Interaction energy of a molecule with one periodic electric field

$$H_{eff} = H^{(0)} - \underbrace{\overline{\mu_{0_i} E_i}}_{=0} - \frac{1}{2}\overline{\alpha_{ij} E_i E_j} - \frac{1}{6}\underbrace{\overline{\beta_{ijk} E_i E_j E_k}}_{=0} - \ldots$$

$\Rightarrow$ **Asymmetric electric field necessary** **2 possibilities :**



"Half-Cycle Pulse" (HCP)



Computations

- **1) Semi-analytical solutions : impulsive limit**
- **2) Numerical solutions of the TDSE (Time dependent Schrodinger equation)**

$$i\hbar\frac{\partial\Psi(t)}{\partial t} = H(t)\Psi(t)$$

Resolution in the basis of the rotational states

Initially $|J,M\rangle$

$P(|J,M\rangle) = e^{-BJ(J+1)/(kT)}$

$\Rightarrow$

$$|\Psi(t)\rangle = \sum c_{J',M'}(t)|J',M'\rangle$$

$$i\hbar\dot{c}_{J',M'} = \sum_{J'',M''} c_{J',M'}\langle J',M'|H(t)|J'',M''\rangle$$

Impulsive limit

$$\Psi(t) = U(t_0, t)\Psi(t_0)$$

$$H = H_0 \Rightarrow U(t, t_0) = e^{-i\, H_0 (t - t_0)/\hbar}$$

$$U(t, t_0) = e^{-i/\hbar \int_{t_0}^{t} H_0 dt'}$$

Impulsive limit approximation : case of a time-dependent Hamiltoni

$$U(t, t_0) \approx e^{-i/\hbar \int_{t_0}^{t} H(t') dt'}$$

Our case : $T_p \square T_{rot} = \frac{\pi\hbar}{B}$

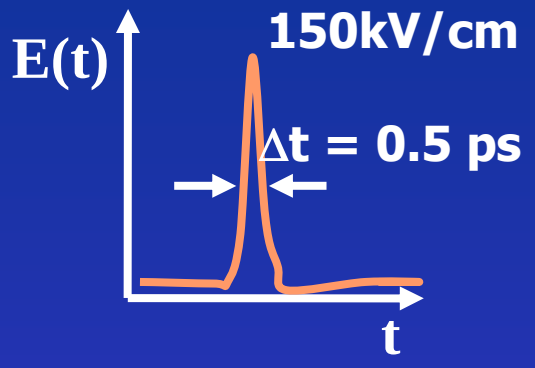
ur case : equivalent to neglect the rotation of the molecules during the interacti

Momentum kick

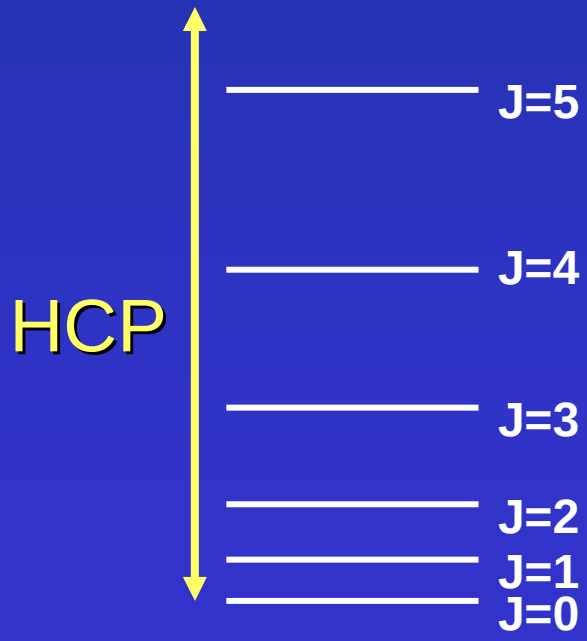
$$U(t, t_0) \approx e^{-i/\hbar \left(-\mu_0 \, Cos\theta \int_{t_0}^{t} \mathrm{E}(t') dt' - \frac{\Delta\alpha}{2} Cos^2\theta \int_{t_0}^{t} \mathrm{E}^2(t') dt' + ... \right)}$$

Dion et al., EPJD 14 : 249 (2001)

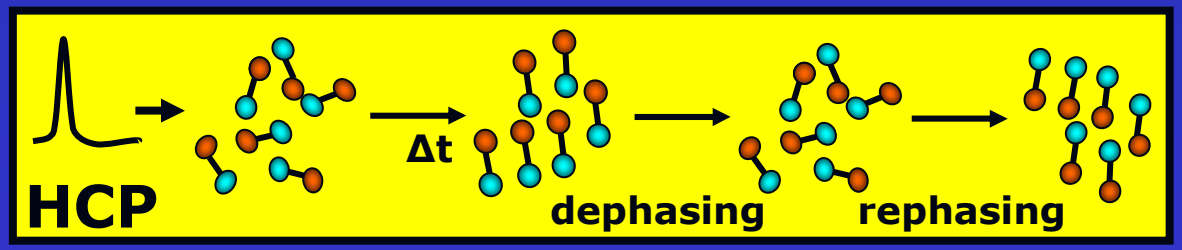
Transient Field-Free Orientation of Polar Molecules



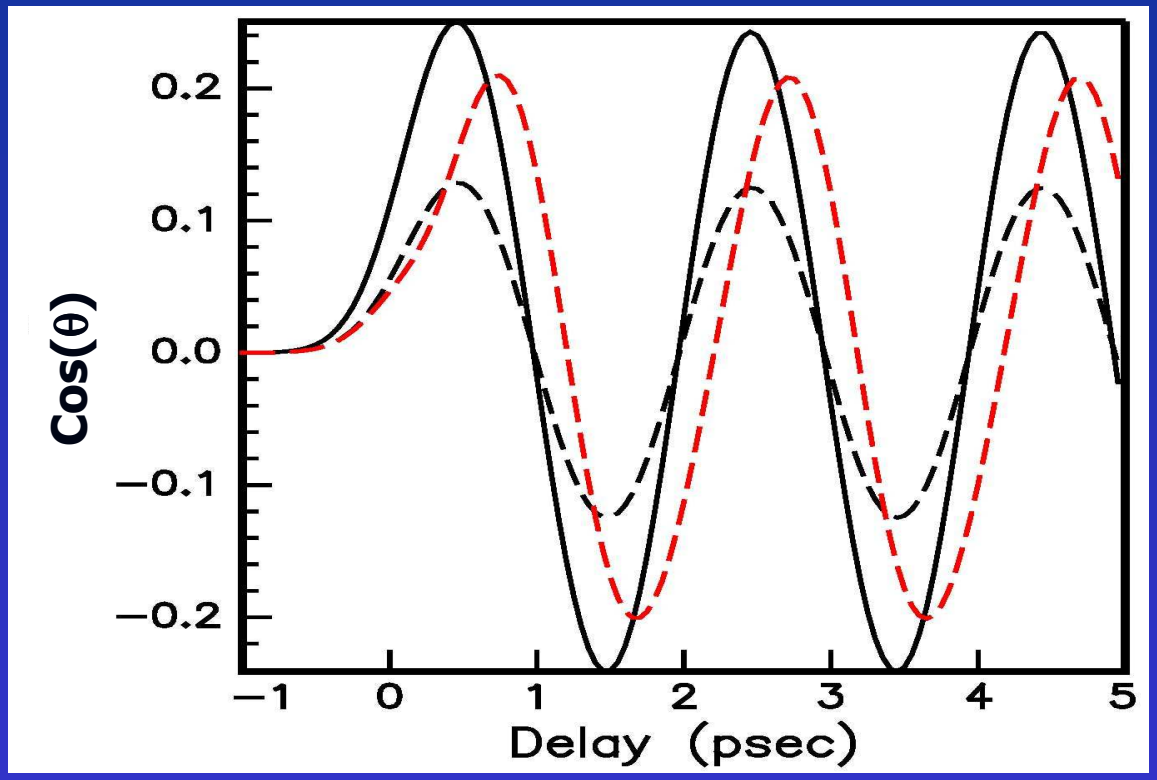
Half-Cycle Pulse



$$H(t) = -\mu_0 E(t)\, Cos\theta$$



HBr T = 2K

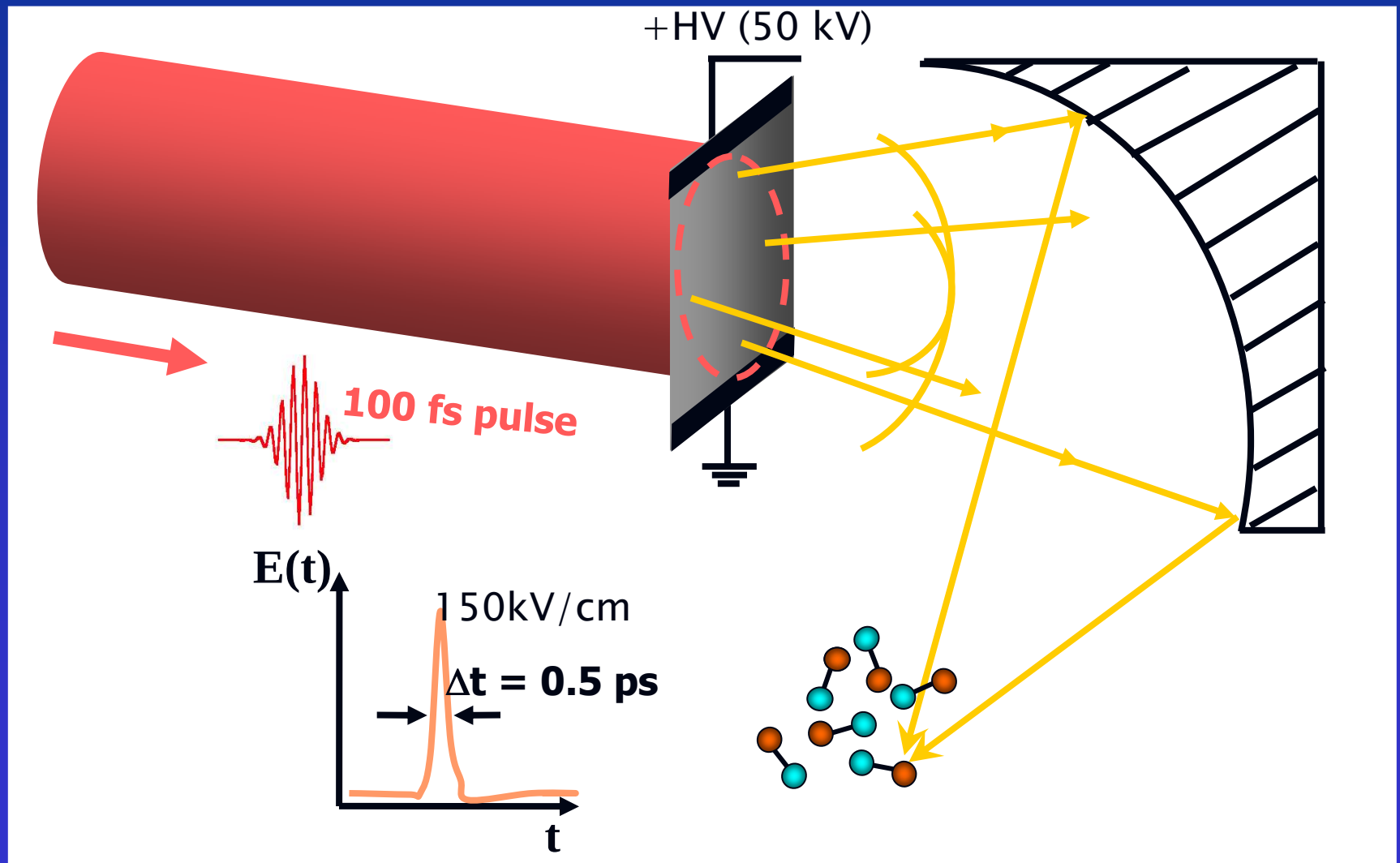


150kV/cm

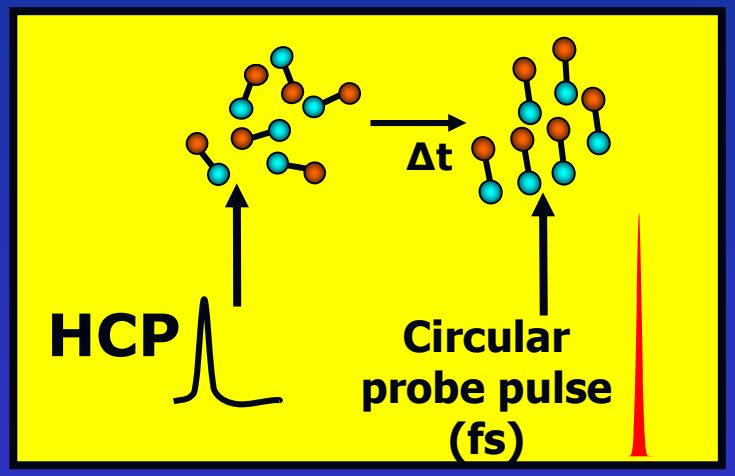
300kV/cm

150kV/cm
+
800 nm

HCP generation

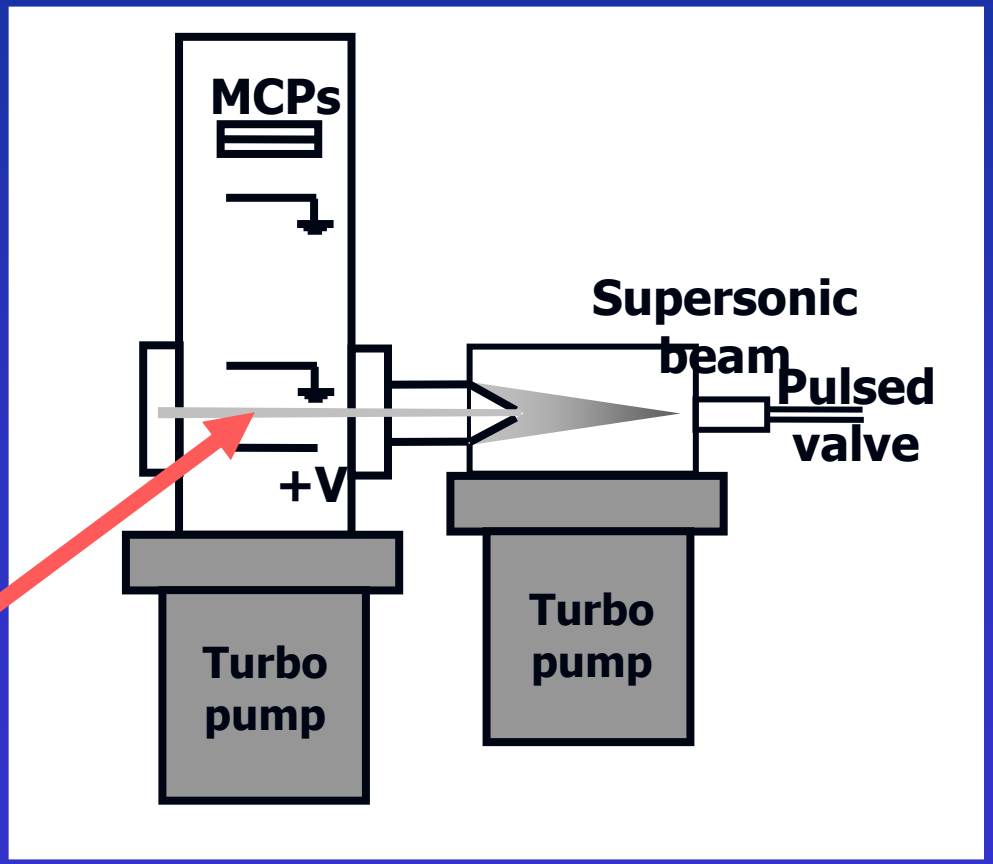


Experiment



Ex :
Hydrogen Bromide (HBr)
$\mu_0 \approx 0.8$ D

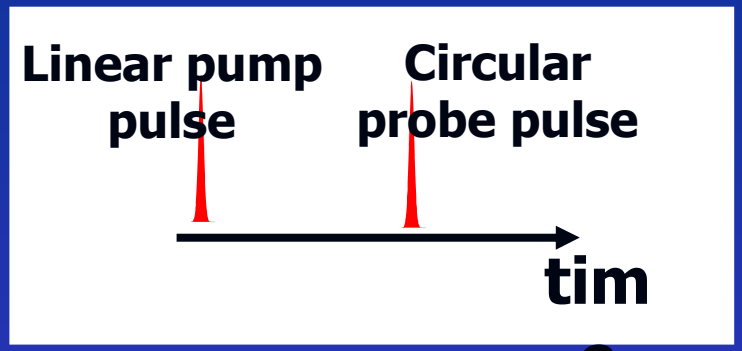
Lasers (780 nm)
HCP

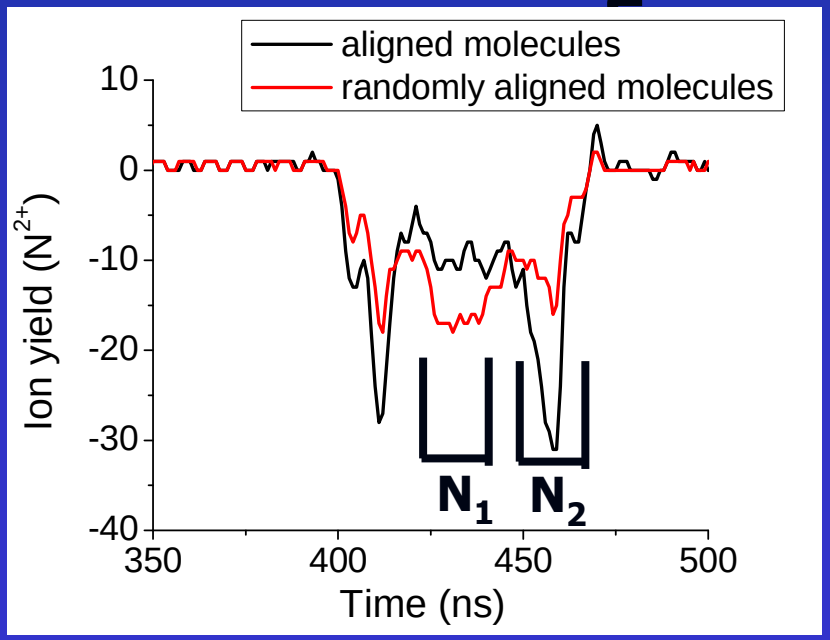


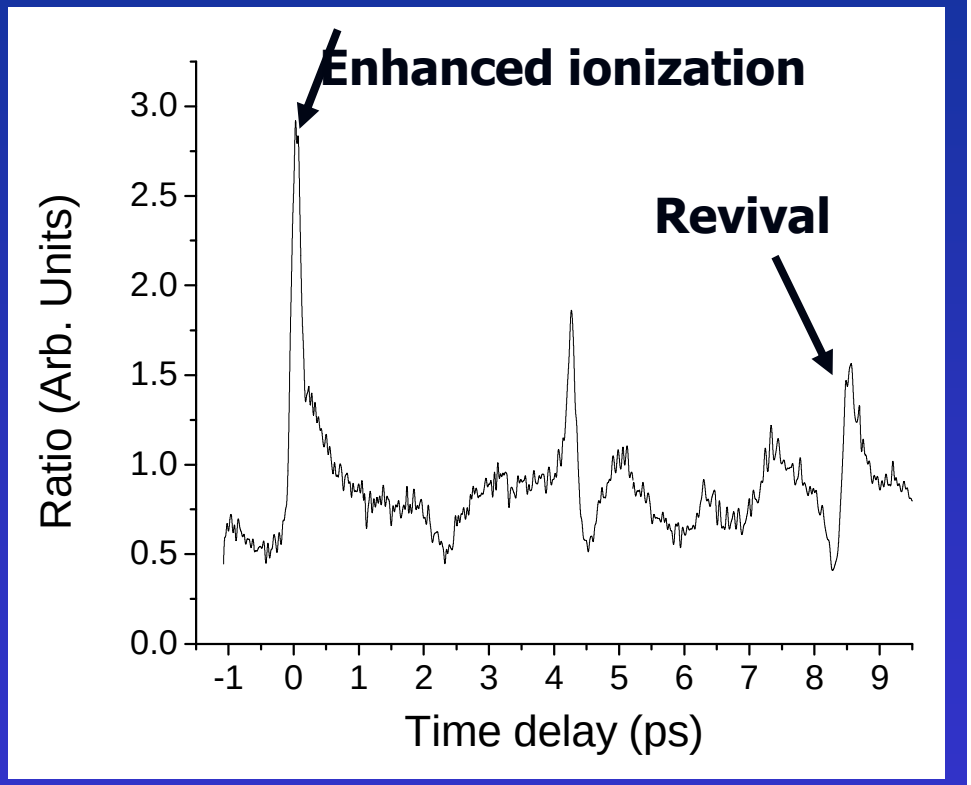
Difficulties

- Synchronization (delay stage)
- Space overlap
- Stabilization (intensities, chirp)
- Calibration of an intense HCP
- Temperature

Alignment : N_2

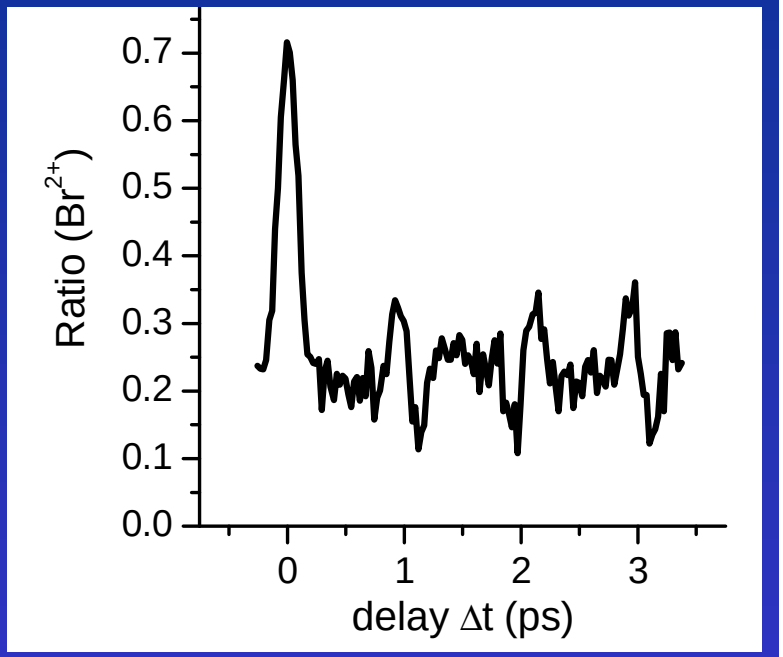


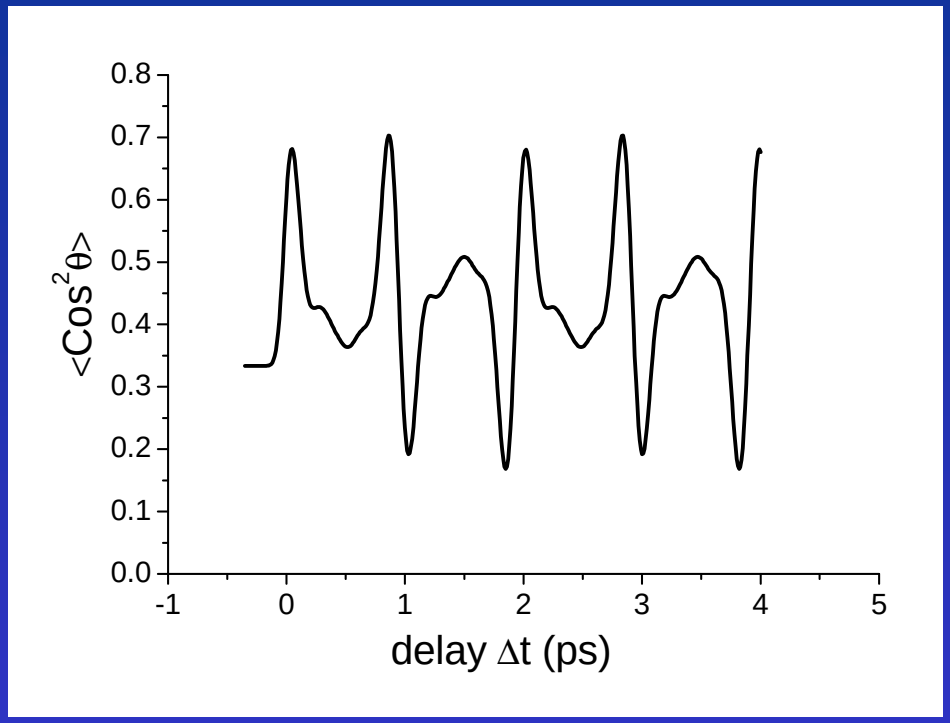




$$\text{Ratio} = \frac{N_2 - N_1}{N_1 + N_2}$$

Alignment : HBr





$\Delta\alpha \approx 1.5$ (a. u.) and $T_r \approx 15$ K

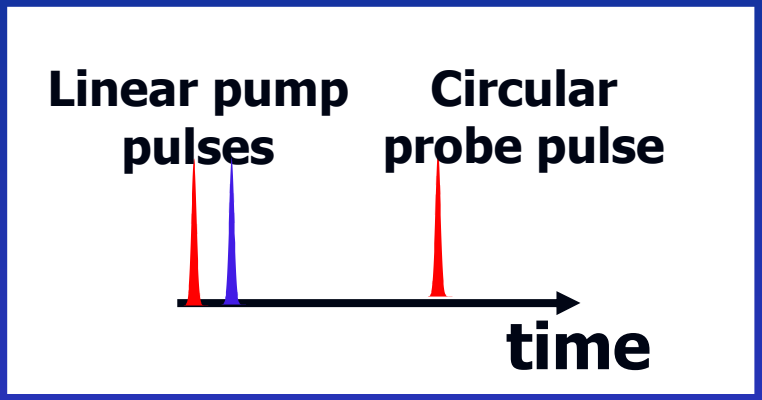
Strong dependence of the degree of orientation with the temperature : we hope to get better !

Orientation with two overlapping femtosecond pulses

$$E(t) \propto Cos(\omega t) + Cos(2\omega t)$$

Promising : possibility to orientate molecules without the need of any dipole moment

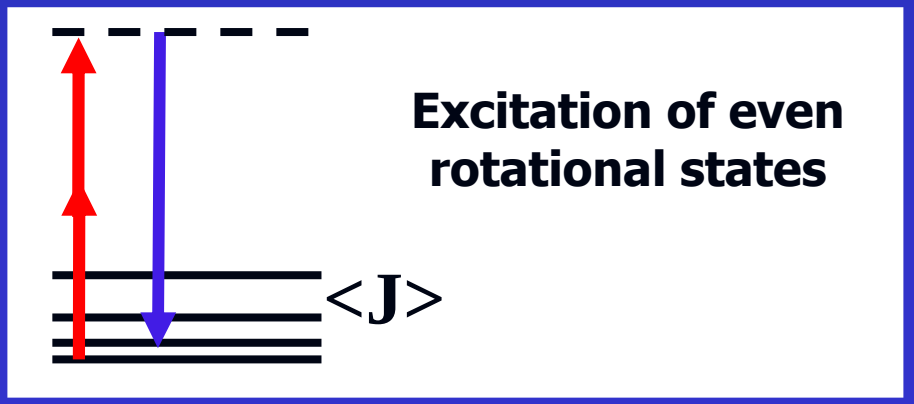
Ex :
Carbon monoxide (CO)
$\mu_0 \approx 0.12$ D



Parity of a $|J,M\rangle$ state is $(-1)^J$

$\Rightarrow$ ***Even and odd J states population necessary***

$$|\Psi(-\vec{R})|^2 \neq |\Psi(\vec{R})|^2$$



Orientation with two overlapping femtosecond pulses

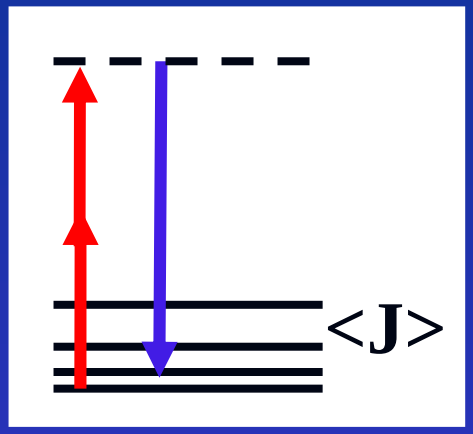
$$H_{eff} = \overline{\frac{1}{2}\alpha_{ij} E_i E_j} - \overline{\frac{1}{6}\beta_{ijk} E_i E_j E_k}$$

$$H_{eff} = -\frac{1}{4}\left(E_\omega^2 + E_{2\omega}^2\right)\left(\Delta\alpha \, Cos^2\theta\right) - \frac{1}{12} E_\omega^2 E_{2\omega}\left(\Delta\beta \, Cos^3\theta + \beta_\perp \, Cos\,\theta\right)$$

$$\Delta\beta = \beta_{//} - \beta_\perp$$

$$\beta_\perp / 3 = \beta_{xxz} = \beta_{xzx} = \beta_{zxx} = \beta_{yyz} = \beta_{yzy} = \beta_{zyy}$$

$$\beta_{//} = \beta_{zzz}$$



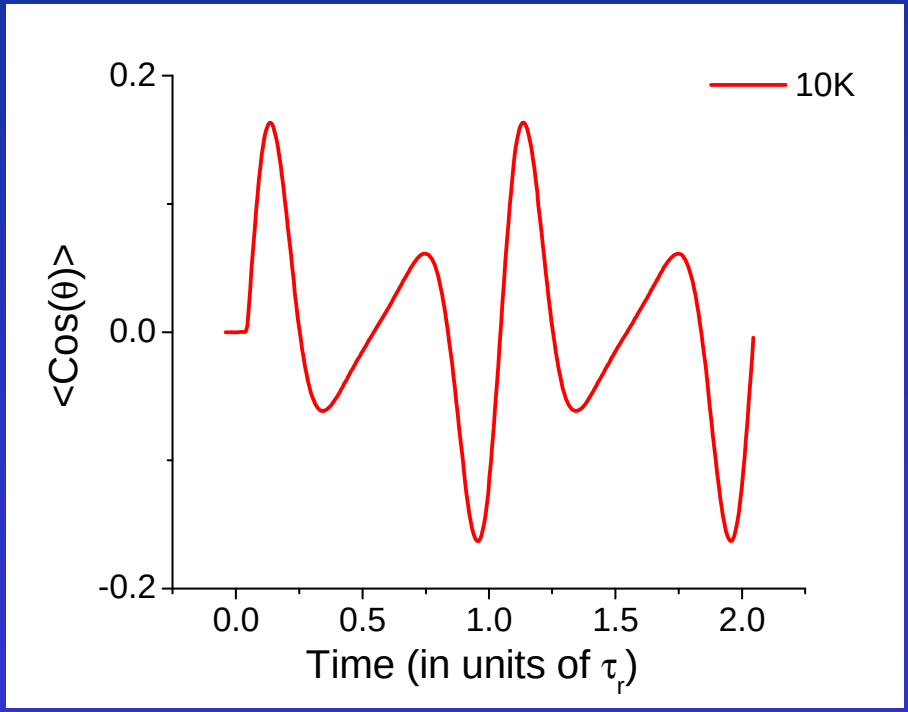
Experimental difficulty : Problems of ionization

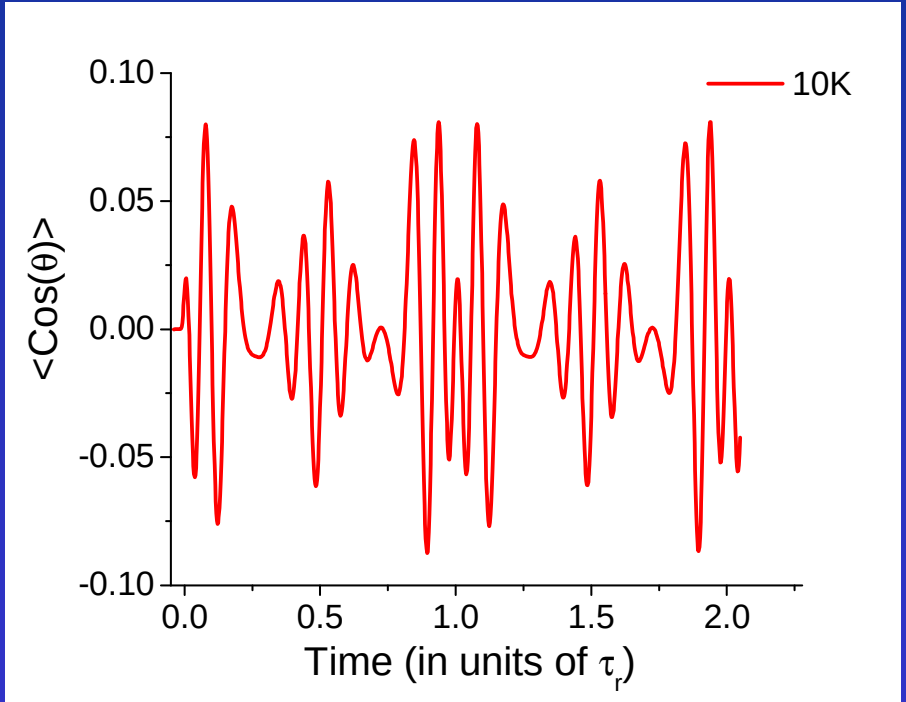
Other problem :
Strong alignment of the molecules (orientation messed up by the alignment)

Possibility to try HBr (polarisability anisotropy 3 times smaller than for CO)

Computations : CO

I = 2.2 10^{14} W/cm^2 in both pump beams



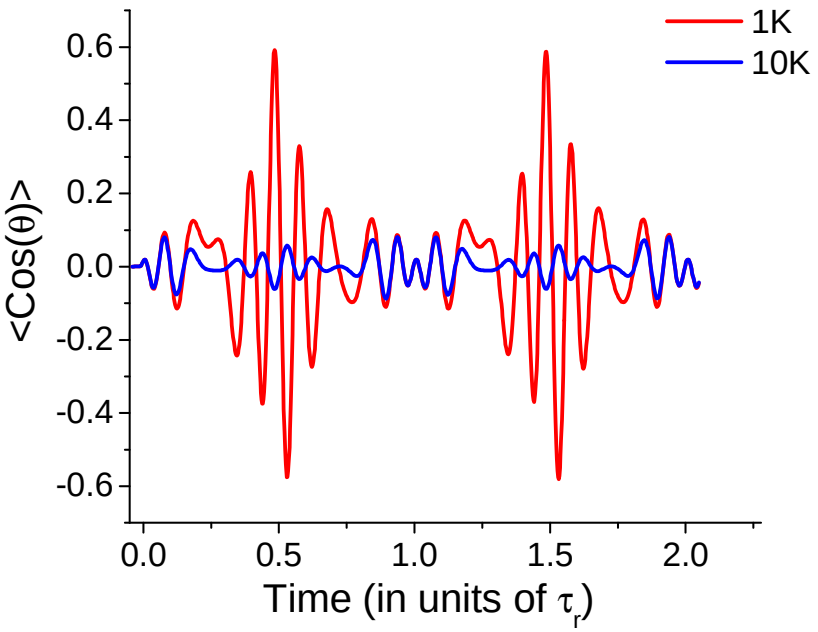


Without alignment

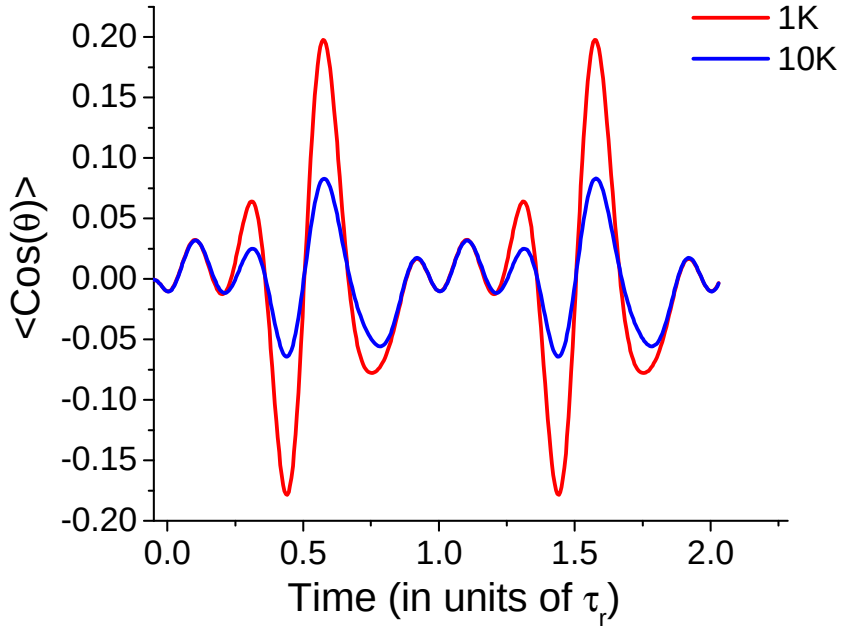
With alignment

Computations

CO



HBr



Very low temperatures necessary !

Conclusion

- Orientation of molecules with electric fields

  Stereodynamics studies, fragments selection...

  but not yet field-free oriented molecules

  Important for recollision experiments, tomographic imaging
- Experimental difficulties with the two overlapping femtosecond pulses (temperature, alignment…)
- Half-cycle pulse ?

Ultrafast Laser / Atomic Physics group

Pr. Robert R. Jones

Dan Pinkham

Xiangdong Zhang

Mary Kutteruf

Brett Sickmiller

Kelsie Betsch

Three-dimensional molecular orientation with combined electrostatic and elliptically polarized laser fields

*PHYSICAL REVIEW A **72**, 063401 2005*

*Haruka Tanji, Shinichirou Minemoto, and Hirofumi Sakai**

Experimental Observation of Revival Structures in Picosecond Laser Induced Alignment of I_2

F. Rosca-Pruna and M. J. J. Vrakking

Phys. Rev. Let. 87,15 (2001)

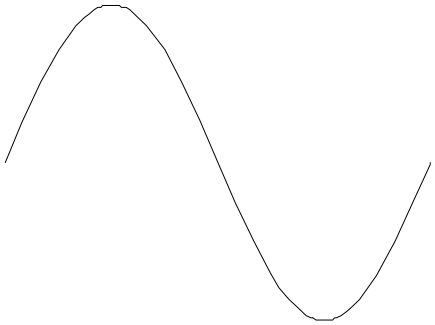
Controlling the Orientation of Polar Molecules with Combined Electrostatic and Pulsed, Nonresonant Laser Fields

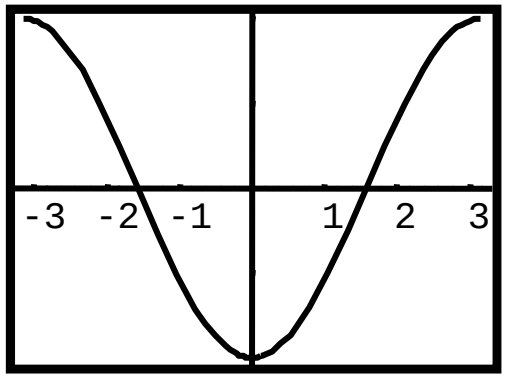
Hirofumi Sakai, Shinichirou Minemoto, Hiroshi Nanjo, Haruka Tanji, and Takayuki Suzuki*

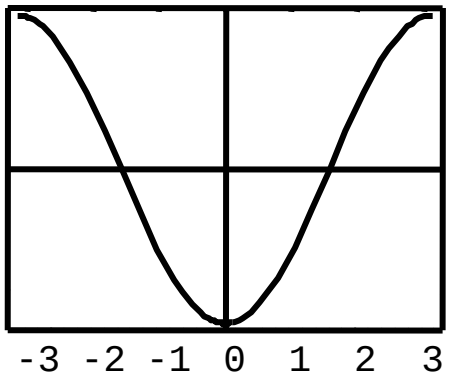
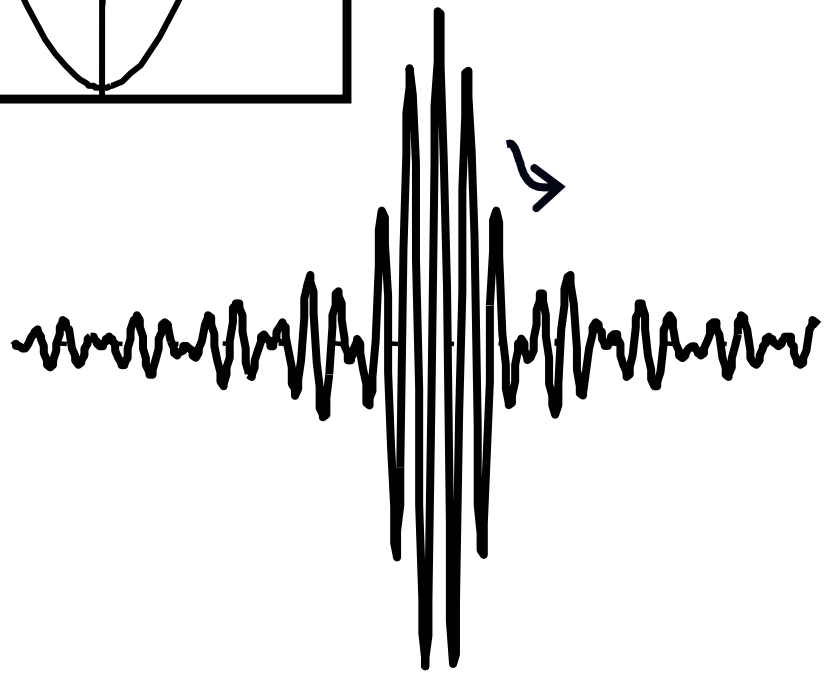
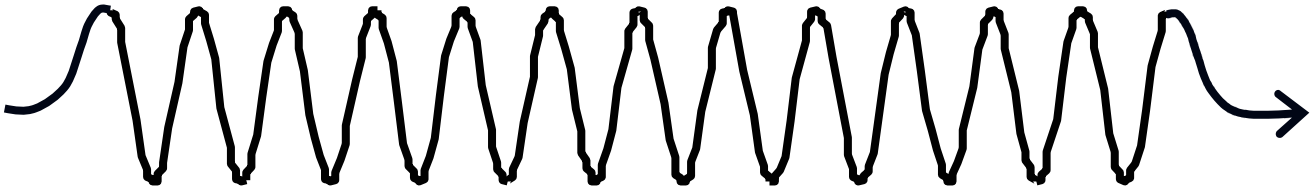
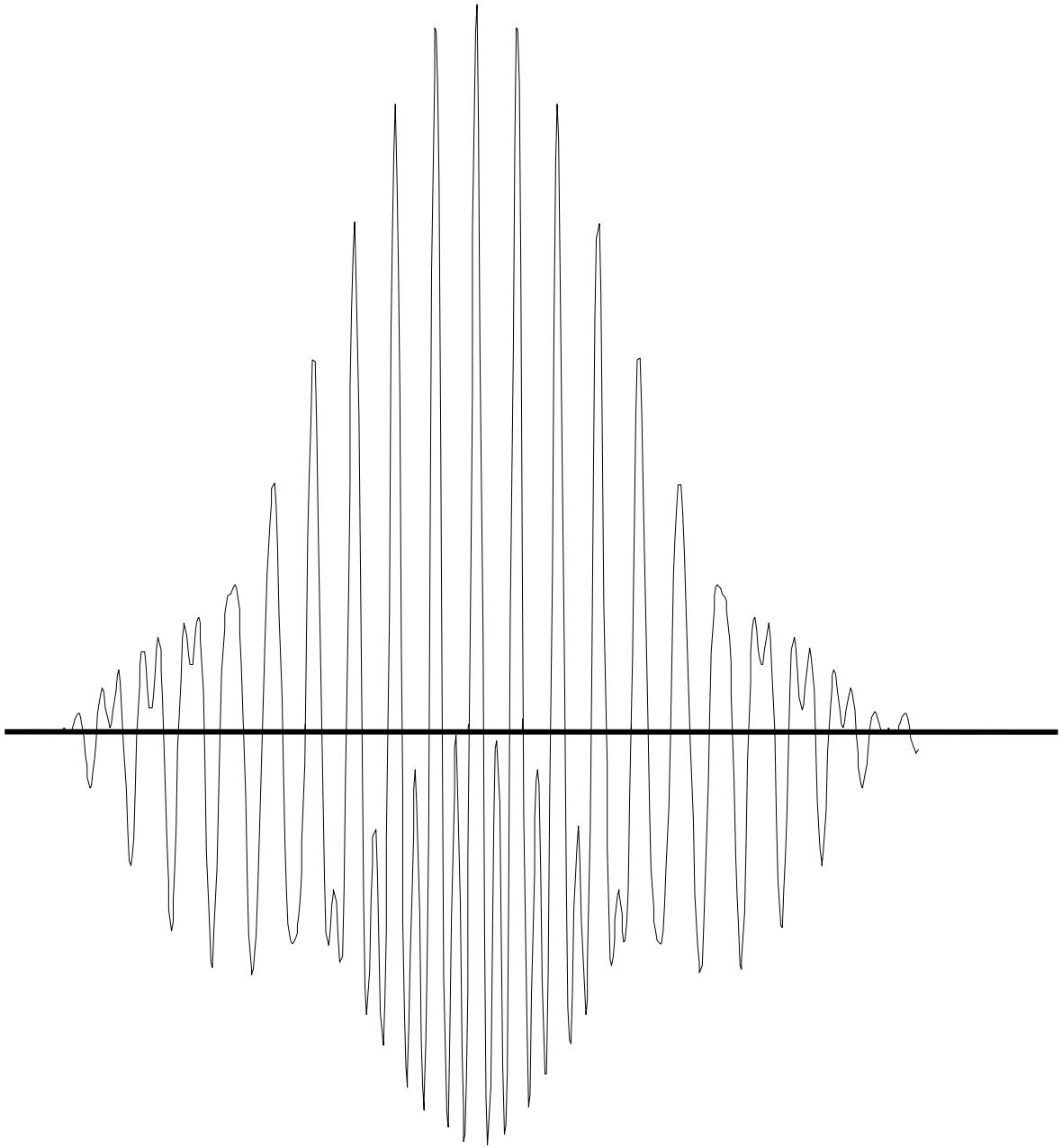
Phys. Rev. Let. 90,083001 (2003)

Photodissociation of oriented HXeI molecules in the gas phase

R. Baumfalk, N. H. Nahler, and U. Buck, J. Chem. Phys. **114**, 4755 (2001).




-3 -2 -1 1 2 3


-3 -2 -1 0 1 2 3